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Condensed Mode Cooling of Ethylene Polymerisation in Fluidised Bed Reactors

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TOC

A survey of the academic and patent literature on condensed mode cooling for the production of polyethylene discuss the impact of adding chemically inert species to the gas phase. In addition to increasing the cooling capacity of the reactor, these supposedly inert substances can change many aspects of the process including the polymerisation rate, polymer properties and reactor stability.

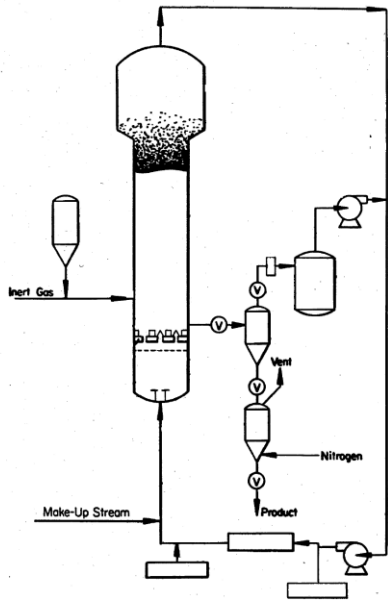
Abstract

This review gives an overview of the evolution of the technology of condensed mode cooling, primarily for the case of ethylene polymerisation on supported catalysts in fluidised bed reactors. It is well known that this mode of heat removal is quite effective in allowing polyolefin manufacturers to increase significantly production rates. What is perhaps less well understood are all of the issues that, in addition to the effect of the latent heat of vaporisation of injected liquid components, also have an impact on the rate of production and behaviour of the reactor. However, the liquid components injected into the reactor can vaporise rapidly under full scale conditions, leaving behind several heavy components (with respect to ethylene) that have numerous effects on how the particles behave, on the reaction rate, and on fluidisation, fouling and other parameters related to reactor and process performance.

Key Words

Condensed Mode Cooling, Gas Phase Ethylene Polymerisation, Fluidised Bed Reactor, Supported Catalyst, Heat Transfer

Figure for Abstract



Schema from US Pat. 4 543 399 describing what is often referred to as the original condensed mode of operation for ethylene polymerisation.

1 Introduction

The commercial importance of polyolefins in general, and polyethylene in particular is undeniable. Polyethylene (PE) is the mostly widely produced polymer on the planet in terms of volume. It can be made either by a free radical process, leading to low density polyethylene (LDPE), or via different catalytic routes in solution, gas and slurry phase processes. In the current review we will focus entirely on gas phase processes (i.e. processes in which solid, growing particles are suspended in a continuous vapour phase) for ethylene polymerisation on supported catalysts; the interested reader is referred to reference [1] for more on other process and reactor designs, an overview of catalyst technology, as well as on the fundamentals of olefin polymerisation.

In order to understand the economic importance of gas phase processes, let us briefly consider the size of the market for the two most widely used technologies^[2]. According to a recent presentation by Univation, in 2012 the Unipol™ gas phase process is used in over 130 licensed production lines around the world with an installed capacity of 32 million tonnes/year of polyethylene^[3]. Innovene™ G, the second most widely licenced gas phase technology appeared to have an installed annual capacity 5-7 million tonnes at the same time^[4,5]. On the whole, if we add in other PE producers, gas phase processes are used to make well over 40 million tonnes annually.

The reason for this success is that over the course of the past 60 years, tremendous progress has been made in catalyst performance, allowing producers to tailor properties and increase catalyst yields such that it is possible to make on the order of several 10s of kilograms of PE per gram of supported catalyst being possible. However the use of such highly active catalysts has imposed a certain number of process challenges, not the least of which is preventing overheating from what is a highly exothermic reaction. Overheating can lead to problems of product quality (molecular weight, composition, catalyst deactivation...), the formation of lumps if the particles become stickier, poor fluidisation, dome sheeting (the formation of sheets on the walls of the disengagement zone that can fall back into the reactor^[6]), etc. Furthermore, product quality is a function of the reactor temperature, so one needs to be able to remove the heat *and* to control the reactor temperature T_R . Different strategies and specific reactor designs for the polymerisation of ethylene on supported catalysts have been developed to overcome problems related to heat removal.^[1]

This last point, which is the focus of the current article, is an extremely important one; in fact it is not unreasonable to say that heat removal is the number one factor that limits the rate of production of PE on an industrial scale. A rough calculation from Soares and McKenna^[1] shows that a modest production line (200 kT/yr – small by the standards of today) generates on the order of 25 MW of heat from the polymerisation alone. If one considers that the melting point of a typical linear low density polyethylene (LLDPE) is on the order of 110°C, and that a typical operating temperature in an industrial reactor is 85-95°C, there is very little margin for error in terms of heat removal.

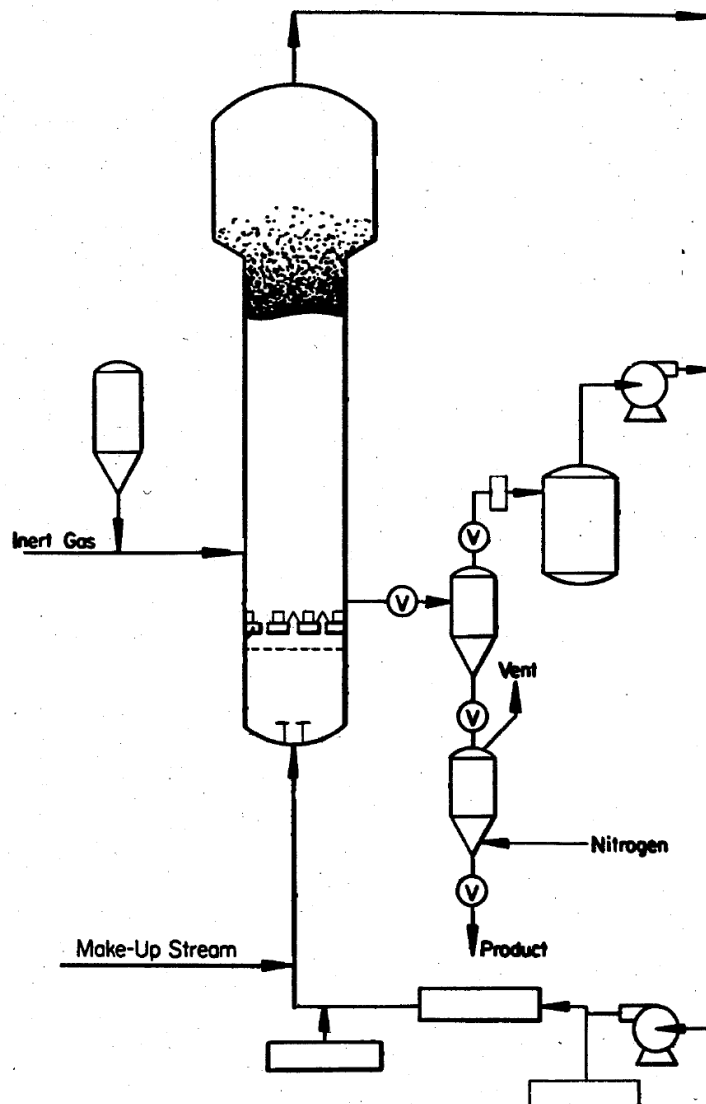


Figure 1. Schema of a typical fluidised bed reactor with peripherals for ethylene polymerisation. [13]

In fact, for reasons essentially linked to heat removal, the only type of reactor currently used to polymerise ethylene in gas phase reactions is a fluidised bed reactor (FBR), an example of which is shown in the schema in Figure 1. Because of the sheer scale of production, these reactors are operated continuously. The reactor is a cylinder with a enlarged section at the top. The diameter of the main section of the reactor is on the order of 2-6m, the height of the main cylindrical section from 10 to 20m, with the dome adding an additional few metres. The purpose of the dome is drop the linear velocity of the gas with the goal of causing any small particles that are blown out of the main bed to become defluidised and fall back into the main bed. Ideally, the reaction takes place inside the main cylindrical portion of the reactor. Here, a constant stream of fluid (either a gas, or a mixture of gas and liquid droplets) is fed into the bottom of the FBR where it passes through a gas distributor at a velocity high enough to fluidise the polymer particles containing the active sites of the catalyst.

Note that other configurations are possible for FBRs. For example, it is possible to withdraw the reactor powder from the bottom of the reactor, and recycle a (significant)

fraction of it to the top of the powder bed,⁷ agitate the bed, or use an internal draft tube to promote internal circulation patterns.⁸ However, the discussion of different FBR designs is outside the scope of this publication; for the purposes of understanding condensed mode operation and its implications, we will limit our consideration to the FBR described above.

A continuous stream of fresh catalyst or prepolymerised particles is fed to the bed, typically near the distributor plate, and at least one stream of polymer particles is withdrawn from the bed. The height of the powder bed will depend on many factors such as the production rate, particle morphology etc., but it is usually at least a couple of metres lower than the total height of the cylindrical portion of the bed. Typical FBR operation entails keeping a reasonably constant bed height. As shown in Figure 1, the polymer particles withdrawn from the reactor pass through at least 2 discharge chambers where absorbed process gases are evaporated and sent to the recycle. The recycle stream is then compressed and cooled before being sent back into the reactor. (N.B. removing the heat from the recycle stream is the most significant means of cooling the reactor. This point will be discussed in detail below.) As a first approximation, one can consider that the gas stream moves through the bed in roughly plug flow, and that the powder phase of the bed has an residence time distribution similar (RTD) to that of a continuous stirred tank reactor (CSTR). Of course, in reality the real RTD can be significantly more complex, but the CSTR approximation allows one to get an order of magnitude estimate of reactor behaviour.

The role of the distributor plate is to ensure that the incoming fluid is fed as evenly as possible across the diameter of the bed, and to eventually orient the fluid flow. While it is not the object of this paper to discuss details of FBR equipment design, it should be pointed out that the distributor plate is one of the more critical pieces of equipment in an FBR, and can play a very important role in achieving good fluidisation!^[9] It is typically a perforated plate (although it could also be a screen or slotted plate) similar to a bubble cap tray one finds in a distillation column, that contains an array of holes on the order of 1-2 cm in diameter that are designed to allow the incoming fluid through, while stopping the particles in the bed from accumulating at the bottom of the reactor. These holes can be open, but are typically covered with fixed or hinged caps to ensure that the powder does not fall through^[10], or even covered with projecting nozzles that allow for the spraying of a liquid into the bottom of the reactor^[11].

As mentioned above, the incoming upward-flowing feed fluidises the particles. Typically, the superficial gas velocity (volumetric flow rate of gas divided by the cross sectional area of the reaction zone) is on the order of 0.5 – 1 m/s, and the relative gas particle velocity in the vicinity of 2 – 8 times the minimum fluidization velocity. In order to get such high flow rates through the bed, one typically uses a recycle ratio upwards of 50, with low per pass conversions (2-30%). The relative particle/gas velocities in an FBR are higher than those found for stirred bed reactors, meaning that convective heat transfer between the particles and the gas phase is more favorable in an FBR than any other type of reactor. Given that heat transfer, in particular heat transfer between the powder and continuous phases, is the controlling factor in FBR operation for PE, this why FBRs are the only reactors used to make polyethylene in the gas phase.^[1]

In order to understand the tools at our disposal, let us consider the simplified enthalpy balance around a gas phase FBR given in Equation 1:

$$\dot{m}_{g,in}c_{pg,in}(T_{g,in} - T_{ref}) - \dot{m}_{g,out}c_{pg,out}(T_{g,out} - T_{ref}) - \dot{m}_{s,out}c_{ps,out}(T_{s,out} - T_{ref}) - UA(T_R - T_W) - Q_{vap} + R_p V_R (-\Delta H_p) = 0$$

Equation 1

Here, $\dot{m}_{g,in}$ and $\dot{m}_{g,out}$ are the inlet and outlet mass flow rates of the process gases, $\dot{m}_{s,out}$ the outlet mass flow rate of solid polymer, $T_{g,in}$ and $T_{g,out}$ are the inlet and outlet gas stream temperatures and $T_{s,out}$ that of the leaving solid stream. T_{ref} is a reference temperature for the calculation of the enthalpy. The heat capacities of the inlet and outlet gas streams, and of the solids stream are given by $c_{pg,in}$, $c_{pg,out}$ and $c_{ps,out}$ respectively. U is the overall heat transfer coefficient, A is the surface area of contact between the reactor wall and the powder bed, T_W is the average wall temperature, R_p is the total rate of reaction per unit volume of reactor bed, V_R the volume of the reactive bed, $-\Delta H_p$ is the overall enthalpy of polymerisation, and Q_{vap} is the total enthalpy change due to evaporation of any liquid in the reactor (it will be the sum of the total mass of each species that evaporates per unit time multiplied by the enthalpy of vaporisation). If we select $T_{ref} = T_R = T_{g,out}$, and make some reasonable assumptions:

- the solid leaves the reactor at the same temperature as the gas;
- the reactor is operating at a steady state with a uniform temperature T_R (we will see below that this last simplification is not strictly true, but these simplifications are acceptable for our purposes) [10,12,13];
- the enthalpy of the catalyst (or prepolymer) feed stream is negligible with respect to the other streams;
- there are no significant heat losses;

then equation 1 can be rearranged to yield:

$$R_p V_R = \frac{\dot{m}_{g,in}c_{pg,in}(T_R - T_{g,in}) + UA(T_R - T_W) + Q_{vap}}{(-\Delta H_p)}$$

Equation 2

Clearly, increasing the productivity of the reactor ($R_p V_R$) at a constant reactor temperature means either allowing T_R to increase and/or increasing the heat removal capacity of the reactor. T_R can be allowed to change within a reasonable range, but in reality the value of the bed temperature is limited by problems of softening and sticking of the particles, and by quality constraints linked to the catalyst performance. It is extremely difficult to increase the value of the overall heat transfer coefficient U given that it is a function of the composition of the reactor contents and the gas flow rate. Recall that the size of the polymerising particles in the reactor can range from a few tens of microns (if fresh catalyst is injected into the reactor) up to a millimeter or so. That renders fluidisation somewhat complex, as the minimum fluidisation velocity is proportional to the particle diameter, d_p , to the power of 1.8 [14,15]. In practical terms, this means that one cannot simply increase the flow rate of gas through the reactor as a means of increasing U .

This basically leaves us with c_{p_i} and the enthalpy change due to the evaporation of any liquid in the reactor as the major levers for increasing the rate of evacuation of energy from the reactor.

It is therefore possible to use the composition and phases of the feed stream(s) (only the inert components obviously) to increase the amount of heat that can be removed and thus the production rate. This is an admittedly over-simplified image of heat transfer in an FBR, nevertheless it illustrates the importance that the evaporation of liquid species can have, and it is this concept that is at the origin of what is often called “Condensed Mode Cooling”.

Before going into a discussion of modern condensed mode operation, it is worth pointing out that the notion of application of the second law of thermodynamics in this context is not new. In fact the concept of using inert liquids to cool reactors where an exothermic reaction is being performed is probably as old as the second exothermic reaction ever performed (during the first one, the experimenters probably burned their fingers on a hot rock and figured out that cooling it with water before picking it up was a good idea). And even in the very specific case of cooling down gas phase olefin polymerisations, liquids have been injected into reactors to control the temperature for decades.

2 A (very brief) history of the development of technology for the gas phase polymerisation of olefins.

The main purpose of this brief technology overview is to help us understand why, and how the development of condensed mode technology came about. The discussion will cover a time frame from approximately the end of World War II to the end of the 1970s. As we progress through the approximately chronological discussion in this section, it should be recalled that catalyst technology was constantly evolving with productivities (and thus heat generation rates) increasing dramatically over the time frame in question. Clearly, it is very difficult to know exactly whether or not a certain number (especially of the older) patents were ever implemented commercially, so the reader should not assume that the following analysis implies that they were unless clearly stated. Rather, this analysis of the patent literature is intended more to help us analyse the evolution of the concept of condensed mode cooling in the polyolefin industry, as well as to understand how the technology is implemented and what the repercussions might be.

The use of evaporation as a means of cooling olefin polymerisations is rather wide spread, and has been for quite some time. One of the earlier examples of this is given in reference [16] that describes a reactor where an $AlCl_3$ catalyst was used to polymerise propylene in solution in a mixture of liquid propylene and propane. The pressure was controlled in such a way that the mixture remained at its boiling point, and the vapour phase was removed, condensed in a reflux condenser and sent back to the reactor as a sub-cooled liquid. This concept was used by many companies in early heterogeneously catalysed polypropylene processes, including by BASF^[17], Sumitomo^[18], Hypol (Mitsui)^[19], and El-Paso^[20], all of which employed stirred bed reactors. This approach worked well for polypropylene since it is straightforward to condense C3 and higher

alkanes and alkenes with industrial cooling water. However it is not economically viable for ethylene at reasonable pressures because it requires much lower temperatures for liquefaction than are available with typical industrial cooling brine.

Numerous patents also discuss the compression and liquefaction of propylene as a means of cooling the gas phase polymerisation reactor. In an early patent to BASF^[21], the authors describe a stirred bed reactor in which nozzles are attached to the agitator shaft and are used to disperse “the monomer in gaseous or liquefied form”. While the only example in this patent discusses ethylene polymerisation, it is more likely that it is intended to cover propylene polymerisation as it states that the recycle stream can be partly liquefied. The main point here is that the gaseous effluent from the reactor is recovered, compressed and recycled, and throttled back into the reactor in sufficient quantity and cold enough that the heat of reaction can be eliminated. A series of subsequent patents from the same group clearly discuss cooling the reaction mass by either spraying the catalyst components in liquid propylene onto the bed^[22], at different places in the bed^[23], or simply spraying liquid propylene into the reactor.^[24,25] In this latter case the liquid is sprayed into the bottom of the bed, and the authors take care to point out that it is necessary to limit the flow rate of liquid monomer into the bed to avoid blowing the reactive powder out of the bed and into the overhead condenser (probably because the stirred powder bed reactor had no equivalent of the dome or disengagement zone common in FBR).

Another patent from Mitsubishi^[26] describes a similar system, but with injection of liquefied monomer above the powder bed as shown in Figure 2a, thereby overcoming problems linked to expansion of the liquid beneath the particles. The liquefied monomer is sprayed in through a sparger at the top of the reactor, where it is then mixed with the contents. Although the examples in the patent treat both propylene and ethylene polymerisation, in order to be injected in liquid form the ethylene had to be cooled to -15°C, so one assumes that this type of process is also intended only for polypropylene on a commercial scale.

A different reactor proposed by Chisso can be seen in Figure 2b. This reactor is a stirred fluidised bed, with monomer vapour being fed through the bottom of the reactor at point **1** below a distributor plate (**2**), and liquid feeds through the ports marked **5**.^[27] An interesting point here is the authors cite not only the use of liquefied propylene (for polypropylene) but also the fact that the injected liquid can be an alkane such as propane, butane, pentane, hexane or heptane, thereby making it possible to cool down ethylene polymerisations as well. In the process described in this patent, prepolymerized catalyst is injected into the reactor and the idea is to inject enough liquid that almost all of the heat of polymerisation can be absorbed. The inventors claim that injecting all of the liquid into the bottom of the FBR can be quite dangerous since, if it expands to quickly, the enhanced vapour flow might blow the particles out of the bed (as with the previous example). In addition, poor distribution of the liquid along the reactor walls or on top of the bed can lead to channelling and defluidisation. One of the claims in the Chisso patent of Figure 2(b) also includes the truncated conical shape of the bed that they claim helps circulate the powder.

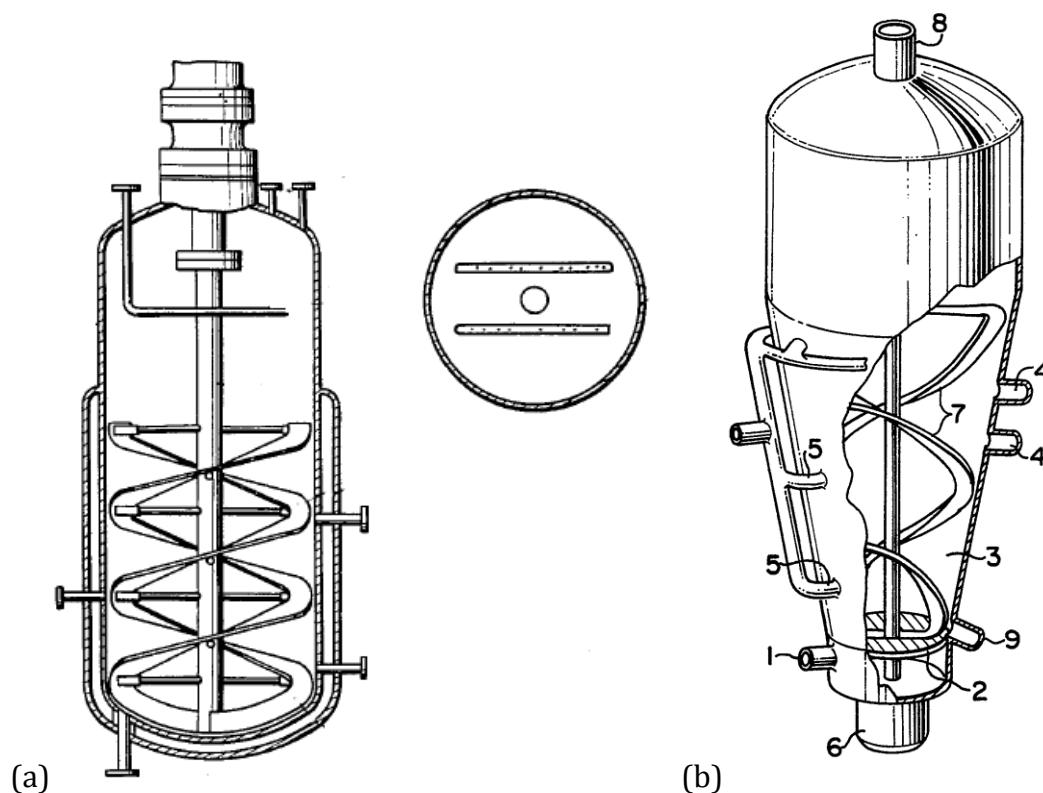


Figure 2. Stirred powder bed reactors (a) from Mitsubishi with liquid monomer feed from the top of the reactor^[26] and (b) a stirred-fluidised bed of similar design from Chisso Corporation with liquid feeds through tubes 5.^[27]

At approximately the same time, a group at Standard Oil developed a different kind of stirred bed reactor, pictured in Figure 3.^[28,29,30,31,32] In this process the catalyst and cocatalyst are introduced at one end and the polymer removed from the other. Monomer, hydrogen and inerts can be fed in as a vapour through separate ports at the bottom of the reactor, allowing the operator to control the concentration profiles along the length of the reactor. A quench liquid is sprayed onto the bed from nozzles along the top of the horizontal cylinder. As with the previous patents, liquid propylene can be used as the quench liquid for temperature control. In a manner similar to the Chisso process in reference [26], iso-butane and iso-pentane can also be used as quenches for ethylene polymerisation. The inventors clearly state that in the case of ethylene polymerisation up to 50% of the heat of reaction can be evacuated using the quench liquid, however the authors of this patent also say that it is desirable to keep the bed dry, undoubtedly to prevent mud formation or agglomeration this will place a limit on the quench feed flow. Apparently up to 90% of the heat of polymerisation can be removed when propylene is polymerised and quenched with liquid propylene. Presumably this reflects more a difference in the rate of heat generation than anything else, as the molar heat of vaporisation of propylene is lower than that of butane or pentane. In other words, it is more difficult to remove all of the heat of polymerisation in a stirred powder bed in the case of ethylene polymerisation than of propylene polymerisation.

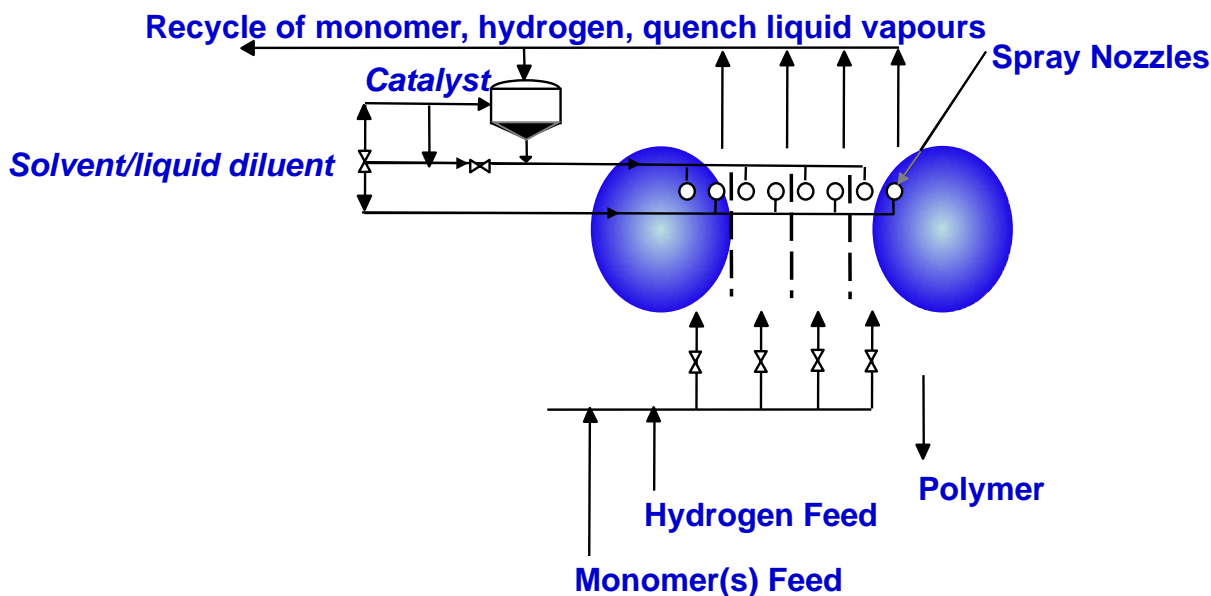


Figure 3. Schematic of the horizontal stirred bed developed by Standard Oil for ethylene and propylene polymerisation.^[28]

This last point appears to be very important: it is more difficult to remove all of the heat generated during ethylene polymerisation than during propylene polymerisation. This appears to be one of the more important driving forces behind the development of the use of the fluidised bed reactor (FBR) for olefin polymerisation. Note that all of the previous examples used a catalytic system of $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ and triethylaluminum (TEA), solutions of which are injected separately into the reactor. While it is difficult to get an accurate picture of the exact value of catalyst productivity, it is well known that during the period from the late 1950s to the late 1960s/early 1970s, the productivity (and thus heat generation rate) of polymerisation catalysts increased by one to two orders of magnitude.^[2,33]

All of these reactors relied on mechanical agitation to move the particles, and to evenly distribute the liquid injected into the bed in order to prevent the formation of large agglomerates. However, starting in the early to mid 1960s, we begin to see the evolution of reactor technology moving from stirred powder beds to different types of FBRs. In 1961, Phillips petroleum was issued a patent for the fluidised bed (and polymerisation process) shown in Figure 4.^[34] Already at this time, the authors were stressing the use of the fluidised bed as a means of enhancing heat removal, and the ethylene feed stream contained just over 20% v/v of ethane, already invoking the concept of dry mode cooling (see following sections).

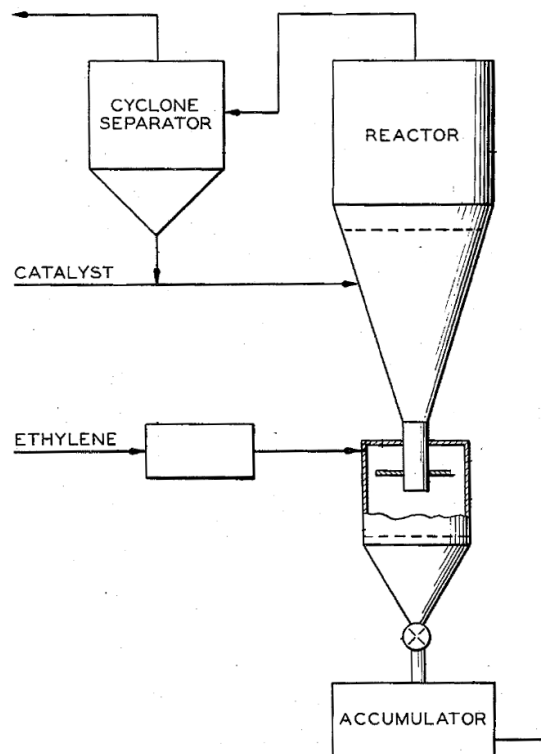


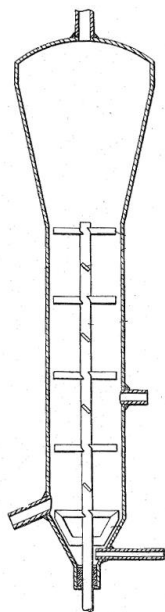
Figure 4. Early FBR from Phillips for polymerisation of ethylene on Cr catalysts.^[34]

Two other early examples of reactors similar to the FBR currently in use are shown in Figure 5. BASF used a chromium catalyst licensed from Phillips in the earliest commercial production of polyethylene in the gas phase, which came on-line in 1964^[2]. This process used the reactor shown in

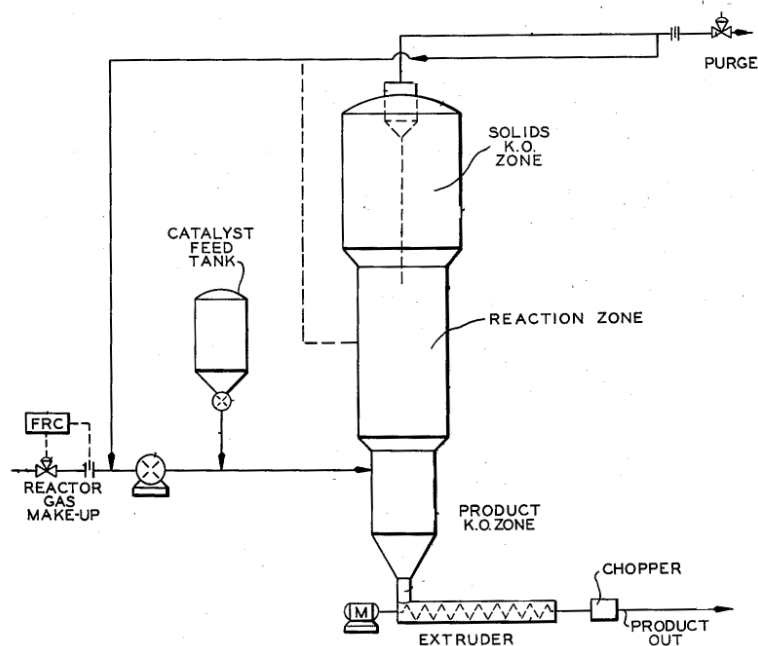
Figure 5 a. ^[35] This reactor has a disengagement zone, but the main reaction zone contains a stirrer to help maintain the particles in a well-mixed or (semi-) fluidised state as the gas velocity was only between 5-15 cm/s – much lower than is currently used in modern processes – and to ensure even distribution of the diluents. Interestingly enough, the inventors suggest that liquid monomers or alkanes can be supplied to the bottom of the vessel with the monomer feed. One of the examples relevant to HDPE production cites the injection of liquid pentane along with the gaseous monomer, and another discloses the use of liquid propylene for polypropylene production. Although the reactor was used commercially for HDPE, it is not clear whether or not the early example of condensed mode cooling was used commercially.

One of the earliest patents to reveal a non-agitated fluidised bed with a structure similar to that used on commercial scales at the current time is shown in

Figure 5b. ^[36] Like the BASF reactor, this one does not have a distributor plate, and the product dropped down through the product knock-out (KO) zone before being fed directly into an extruder. It is probable that polymerisation continued in this part of the reactor and undoubtedly would have led to problems of agglomeration and sticking had it been used in a large scale. This reactor was not ever employed commercially, but it demonstrates the use of the “solids knock-out zone” (i.e. disengagement zone) at the top of the reactor to eliminate fines from leaving the reactor and entering the recycle loop.



(a) BASF Stirred fluidised bed



(b) Phillips first fluidised bed

Figure 5. (a) A mechanically agitated FBR used by BASF in the first ever commercial gas phase production of HDPE^[35]; and (b) Arguably the first patent on the use of a fluidised bed reactor for ethylene polymerisation.^[36]

However it was Union Carbide Corporation (UCC) who filed the first patent on the use of fluidised bed reactors for the production of HDPE using a silica supported chromium-based catalyst in 1967 (the 1967 patent application was abandoned^[2] and eventually a continuation was published in 1977^[37]) and began to produce gas phase HDPE in 1968. One of the major differences between this and the Phillips patent^[36] is in the design of the product withdraw area, where the product discharge proposed by Dye was inside the reactor, whereas the UCC patent has the discharge separated from the reactor, with a distributor plate dividing the feed from the main area of the bed. Apparently the BASF patent^[35] had a discharge system similar to the UCC patent, but the mechanical agitation in the BASF allowed UCC to differentiate their claim.

By the time reference [37] was published, magnesium-supported catalysts had been discovered, leading to a great increase in the available catalyst activity (so-called 3rd generation Ziegler-Natta catalysts). By this point, a gas flow rate of 3 to 4 times the minimum fluidisation velocity was the only way to obtain reasonable heat transfer conditions via convective heat transfer coefficient between the particle and the gas phase of the reactor much higher than those obtained in the stirred bed reactors. A survey of the catalyst patent literature by Nowlin^[2] reveals that the average activity under industrial conditions evolved from about 6 kg PE/g Ti/h (1972 patent to Hoechst^[38]) to upwards of 250 kg PE/g Ti/h according to a UCC patent in 1981.^[39] This of course means that the quantity of heat that one needed to remove per unit volume was also multiplied by over 400%, and that it was becoming more and more important

to develop means of removing heat from olefin polymerisation reactors (and in particular from those operating in the gas phase).

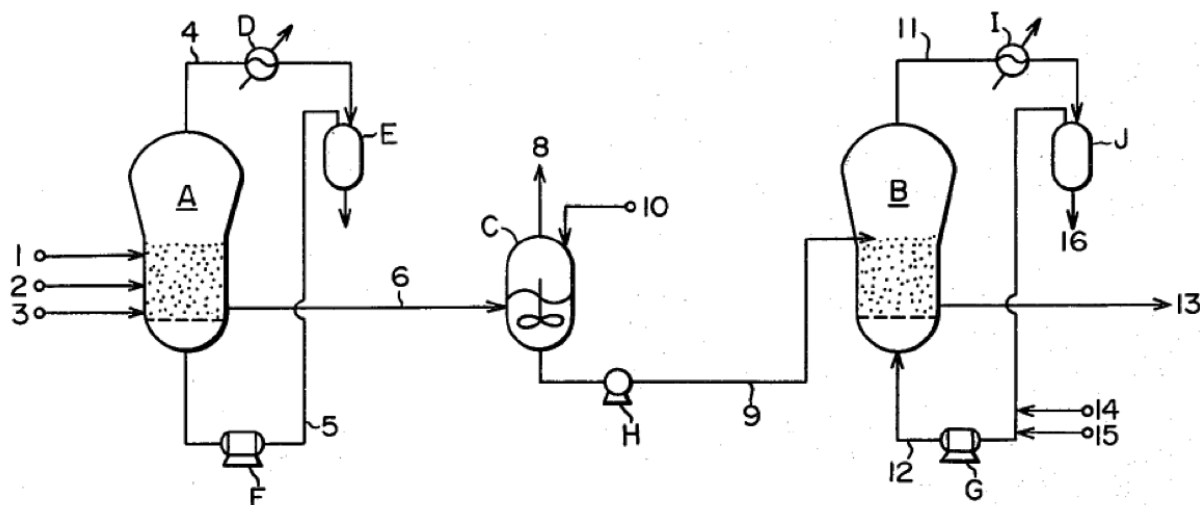


Figure 6. 2 FBR cascade for the production of bimodal (or broad) MWD PE, separated by a slurry tank (C).^[40]

Thus, starting in the late seventies and early eighties more and more focus was put on just this point. Mitsui appears to have been active in this field quite early. One patent describes the use of explicitly adding an ICA (butane in the case of the patent example treating ethylene polymerisation) that is liquefied before being sent to a stirred powder bed reactor for the removal of the heat of reaction.^[41] Although the patent claims that this can be done in an FBR, no examples illustrate that particular means of operation. As an example specific to the gas phase polymerisation of ethylene in modern FBRs, a patent to Mitsui^[40] reveals a process for the production of bimodal (or very broad MWD) PE. It can be seen from the schema in Figure 6 that the 2 FBRs are separated by a tank (C in the Figure). The PE leaving reactor 1 is fed to this tank, along with a liquefied alkane (typically n-butane). The purpose of this tank is nominally to help remove the hydrogen injected in reactor 1 in order to better control the MWD in reactor 2. However, the slurry in this tank contains an appreciable level of alkane, at approximately 300 g PE/L n-butane at 30°C, and when the slurry is fed to reactor 2, the evaporation of the alkane will most certainly contribute to absorbing the enthalpy of the reaction in this second step. Another patent from BP chemicals outlines a similar system, using a volatile alkane in the intermediate tank to facilitate transfer from one reactor to another.^[42] Yet another example, this time for the gas phase polymerisation of isobutylene, refers directly to compressing the gas phase recycle stream, condensing unreacted monomer and other hydrocarbons and feeding the mixture back to a FBR.^[43]

This brief discussion is not meant to be an exhaustive look at the evolution of reactor technology for the gas phase polymerisation of ethylene, but rather presents an overview of the changes in reactor technology during the first 2 to 3 decades of development. At this point it should be clear that the only way to economically polymerise ethylene in the gas phase with highly active catalysts is in a fluidised bed reactor, resembling the one shown in Figure 1. As a point of interest, we can also note that while FBRs are used to make polypropylene (and copolymers of ethylene and

propylene), several of the stirred bed reactors that are no longer viable for ethylene polymerisation are still used for polypropylene – again because at similar production rates the volumetric heat generation rate in a PP process will be about 33% less than in a PE process, and the melting point of PP is much higher than that of PE (about 171 °C for PP vs. approximately 110-140°C for most PE).

In addition to learning that the FBR is the only economically viable gas phase reactor technology for commodity PE, we have also seen that the concept of using liquefied monomer (in the case of propylene) or linear alkanes to cool down gas phase reactions also predates the notion of “condensed mode” operation defined in the Jenkins III patents.^[12,45] Nevertheless, a majority of the reactors where evaporative cooling was used to control the reactor temperature relied on mechanical agitation to avoid lump formation and perturbations to the smooth operation of the reactor, and to ensure smooth operation of the reactor in the face the rapid expansion of liquid entering the reactor. Henceforth we will use “condensed mode cooling” (and related terms) to describe processes patented since the mid-1980s.

3 Fundamentals of Condensed Mode Cooling in Modern PE Plants.

Before proceeding further with the discussion, let us define some terms we will in the following discussion:

Dry Mode (DM) refers to the operation of an FBR where the recycle stream might contain alkanes of a nature and quantity that cannot be condensed by standard cooling water (e.g. ethane).

Super Dry Mode (adapted from reference [44]; SDM) is similar to dry mode, but the recycle stream also includes an alkane with 4 to 6 carbons in vapour form.

Condensed Mode (CM) operation refers to the case where the feed to the FBR contains less than 20% (by weight) liquid. It is like SDM, but the recycle stream is cooled below its dew point.

Supercondensed Mode (SCM) operation is much like condensed mode, but with more than 20% by weight liquid in the feed.

While there are some specific technical differences between condensed^[12,45] and supercondensed^[46,47,48] mode (e.g. in terms of injecting liquid, and reactor operation), the distinction between the two appears to be more a question of quantity of liquid, and the chronological order of the respective patents, rather than of a real thermodynamic differentiation; the cut-off between CM and SCM appears to be 17.4 wt% of liquid in the reactor feed, and based on claims in the original Jenkins III patents. Finally, one will also encounter the terms “High Productivity” and “Enhanced High Productivity” (EHP) mode. These latter terms are often associated with the Innovene™ G process currently developed and licensed by INEOS. For the purposes of the discussion in this paper we will use the terms “condensed” and “supercondensed” for all technology platforms, as the major differences at this level appear to be linked more to the technology used for injecting the liquids than anything else.

3.1 Operating in Super Dry Mode

Before concentrating on CM/SCM, we should take a quick look at SDM. Let us once again consider Equation (2):

$$R_p V_R = \frac{\dot{m}_{g,in} c_{pg,in} (T_R - T_{g,in}) + UA(T_R - T_W) + Q_{vap}}{(-\Delta H_p)} \quad \text{Equation 2}$$

The change of enthalpy of the fluid stream is given by the term $\dot{m}_{g,in} c_{pg,in} (T_R - T_{g,in})$. If one significantly increases the fluid flow rate of the feed stream, it is likely that this will cause significant problems of fluidisation and can lead to fines entrainment. In the event that the inlet fluid temperature is greater than the dew point of said stream, Q_{vap} will be equal to zero, and the only way to increase the productivity will be by increasing the heat capacity of the feed stream. This can be done by adding inert species, such as alkanes to the feed stream. If we consider the data in Table 1, it is obvious that if one were to replace nitrogen as an inert species by another alkane the heat capacity of the gas phase will increase. In addition, as the solubility of a species in amorphous PE increases (longer, less branched), so does its heat of vaporisation (N.B. these values will be a strong function of T and P, and can change under conditions at, or above the critical point).

Table 1. Heat capacities of gaseous components commonly used in the polymerisation of ethylene.

Component (gaseous)	Heat Capacity (25°C) (cal·K ⁻¹ ·mol ⁻¹)	Heat of Vaporisation (25°C) (Kcal·mol ⁻¹)	Solubility in PE (g ICA/100g PE)*
Propylene	15.3 [Erreur ! Signet non défini.]	4.7 [Erreur ! Signet non défini.]	
Propane	17.4 [Erreur ! Signet non défini.]	4.8 [Erreur ! Signet non défini.]	0.29 [58]
1-butene	20.6 [Erreur ! Signet non défini.]	6.0 [Erreur ! Signet non défini.]	
<i>n</i> -butane	23.3 [Erreur ! Signet non défini.]	5.8 [Erreur ! Signet non défini.]	0.94 [58]
<i>iso</i> -butane	23.1 [Erreur ! Signet non défini.]	5.1 [Erreur ! Signet non défini.]	0.77 [58]
Cyclobutane	16.9 [Erreur ! Signet non défini.]	5.7 [Erreur ! Signet non défini.]	1.26 [Erreur ! Signet non défini.]
1-pentene	26.2 [Erreur ! Signet non défini.]	6.9 [Erreur ! Signet non défini.]	
<i>neo</i> -pentane	28.9 [Erreur ! Signet non défini.]	5.4 [58]	1.18 [58]
<i>n</i> -pentane	28.6 [Erreur ! Signet non défini.]	6.6 [Erreur ! Signet non défini.]	1.83 [58]
<i>iso</i> -pentane	28.4 [Erreur ! Signet non défini.]	6.5 [Erreur ! Signet non défini.]	1.63 [58]

1-hexene	31.6 [Erreur ! Signet non défini.]	7.8 [Erreur ! Signet non défini.]	
<i>n</i> -hexane	34.0 [Erreur ! Signet non défini.]	7.6 [Erreur ! Signet non défini.]	2.85 [58]

*at 90°C, 1.72 bars ICA, density LLDPE = 0.918 g/cm³

Improvements of due to operating in this manner, i.e. in Super Dry Mode, can be seen from two examples of industrial production data shown in Table 2.^[44] Here, simply replacing the nitrogen in the feed stream (DM, example 1a) with a mixture of ethane and propane (SDM, example 1c) allows one to increase the heat capacity of the gas phase, and thus to remove more heat and operate the reactor at higher production rates. Note that the heat capacity increases by approximately 20%, but the heat removed and productivity increased by over 34%. This will be explained below when we discuss the impact of the cosolubility effect.

Operating in SDM thus allows one to increase the productivity, and avoiding certain (but not all) challenges associated with injecting liquids into the reactor.^[49,50,51] Reference [44] presents a number of examples of SDM where the authors adjust the composition (and thus the dew point) of the feed stream to increase the heat removal capacity of the reactor, sometimes by upward of 80% without liquefying the feed stream. However the in SDM the more heavy components one has in the recycle stream, the higher the dew point of the feed stream will be, and thus there will always be a trade-off in terms of the temperature difference between the top and bottom of the reactor.

Table 2. Comparison of Dry Mode (example 1a) with Super Dry Mode (Example 1c).^[44]

Compound	Example 1a	Example 1c
Hydrogen	5.63	5.63
Nitrogen	31.02	-
Methane	0.5	0.5
Ethylene	45.0	45.0
Ethane	3.0	27.2
Propane	0	6.82
1-Butene	14.85	14.85
Heat Capacity at 25°C (cal·K ⁻¹ ·mol ⁻¹)	10.7	12.8
Heat Removed in Recycle Cooler (10 ⁸ kJ/h)	1.025	1.38
Production Rate (tonnes/h)	28.7	38.7

3.2 Operating in Condensed Mode

In order to go beyond what is possible in SDM it is necessary to drop the feed temperature below the dewpoint of the recycle stream – in this case we will be operating in condensed mode, and the term Q_{vap} is now non-zero. In this case, the

temperature difference ($T_R - T_{g,in}$) will be such one can remove more heat than if operation is in DM or SDM. Furthermore, the more one cools the recycle stream, the less ICA one needs to remove a given amount of heat.^[47] (On the other hand, one runs the risk of accumulating a lot of liquid at the bottom of the reactor if the $T_{g,in}$ is too low and the droplets are not evaporated quickly.)

According to the first two patents that describe what we now call “condensed mode”^[12,45], increased productivity is achieved by “*increasing the removal of the heat of polymerization from the reactor by cooling gases, continuously removed from the reactor, to a temperature below the dew point temperature of such gases and returning the resultant two phase fluid mixture into the reactor to maintain the temperature of the fluidized bed at the desired level.*”^[12]. According to them, “*This assumption was predicated on the belief that the introduction of liquid into a gas phase fluidized bed reactor would inevitably result in plugging of the distribution plate, if one is employed; non-uniformity of monomer concentrations inside the fluidized bed and accumulation of liquid at the bottom of the reactor which would interfere with continuous operation or result in complete reactor shut-down.*” This patent implies that previously, only “dry” FBRs were known for polyethylene, and it appears that some companies went so far as to ensure that even the small amount of liquid injected with the catalyst should be vaporised before the reactor.^[52]

This edict placed severe restrictions on the amount of high boiling monomer like hexene that could be incorporated into an LLDPE product (in fact, this last statement made in the patent leads one to suspect that this improvement might not have been stumbled upon by accident, when someone tried to increase the amount of hexene in the recycle stream, and unintentionally lowered the dew point so that the stream condensed in the recycle heat exchanger). It needs to be pointed out that some of the patents discussed above, in particular reference [43], made it clear that the concept of injecting liquids into the bottom of FBR was not really a new one. Also, while [26] proposed injecting liquid into the FBR, it was along with the powder stream (in the second FBR of a 2 reactor train), and not through the bottom. Nevertheless, it is often accepted that reference [12] is the “starting point” for condensed mode operation for the production of ethylene. Before this point, the use of a condensed component in a non-agitated FBR for making PE was actively avoided.

A schema of a condensed mode process is shown in Figure 7. Here, the feed to the bottom of the reactor below the distributor plate is composed of ethylene, nitrogen, comonomer, hydrogen and at least one *Induced Condensing Agent* (ICA) that is a (partially) liquefied, chemically inert species. An ICA is typically an alkane. Isomers of butane, pentane and hexane appear to be the most common, and are the ones specifically referred to in reference [12]. Some patents also cite the possible use of other chemically inert compounds such as fluorocarbons^[53,54,55], or liquid cryogenics like super-cooled N_2 , CO_2 or other chemically inert compounds^[56] for this purpose, but cost limitations and environmental concerns work against this option. The choice of which ICA to use will

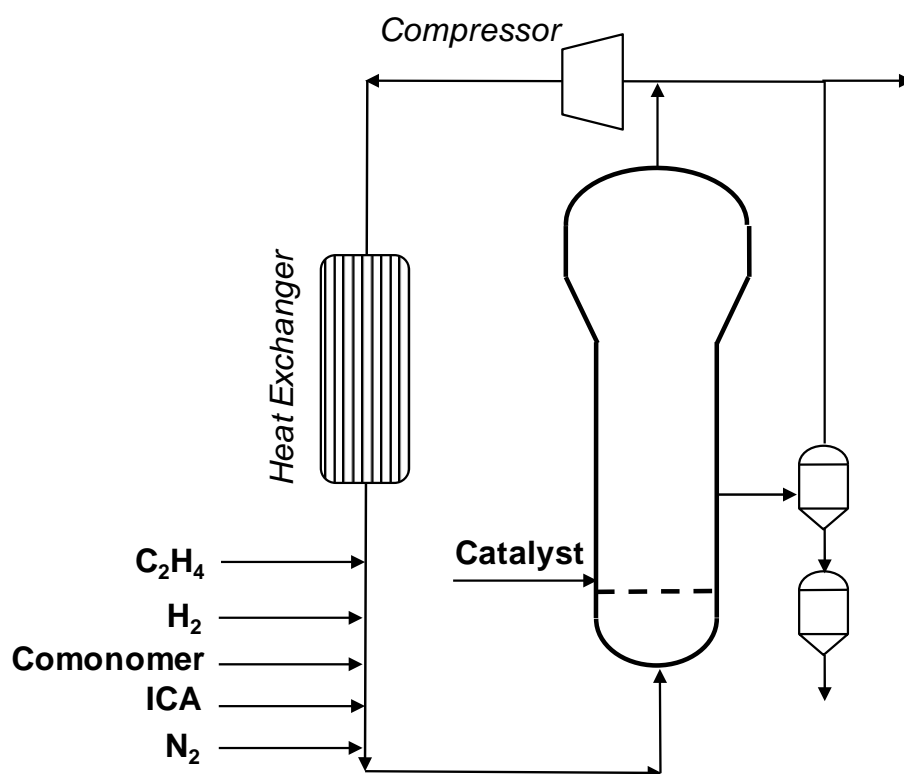


Figure 7. Schema of a gas phase process operating under condensing mode.

depend on a number of factors (we will return for a more detailed discussion of certain of these points below):

Heat Load. The heavier the alkane, the higher the dew point of the recycle stream for a given mole fraction of ICA, the greater the heat capacity, and the higher the heat of vaporisation (c.f. Table 1).^[57] Note that if one prefers to use low molecular weight ICA to avoid stickiness, it is possible to run the reactor at higher pressures in order to put more ICA in the mix.^[58]

Composition. Some inventors claim that hexane is preferred when making 1-hexene LLDPE^[46], possible for reasons to do with monomer/ICA recovery post reactor. The downside of the heavier ICA is increased stickiness of the powders and a heavier load on the downstream purification steps.^[59, 60]

Quality constraints. Typically the dew point of the feed in condensed mode will be from 5-15°C below that of the reactor (rarely more).^[61] If the dew point is too close to the reactor temperature, one runs the risk of stickiness and agglomeration (see below).^[47] While iso-butane and iso-pentane appear to be the most widely used ICAs, in the case where lighter comonomers such as propylene or butene are used, then a heavier alkane is necessary to adjust the dew point of the feed stream accordingly.^[62] Similarly, if one needs to incorporate large amounts of a heavy comonomer such as 1-octene, lighter ICA are required to allow one to increase the comonomer levels to an acceptable level and to keep the approach temperature in a reasonable range.^[47,61] The latter challenge can be more pronounced with Ziegler-Natta catalysts than metallocenes, if the Ziegler catalysts

used do not incorporate high levels of comonomers and thus require more of them in the gas phase.^[47] Since metallocenes require less comonomer than Ziegler-Natta catalysts to produce a given density, one can increase both ethylene partial pressure and the level of ICA in the reactor to compensate for the higher production rates.⁶³

Nature of the polymer. The more amorphous the polymer is, the more susceptible it is to softening and sticking for a given amount of ICA.^[62] Also, the heavier the ICA is, the more it can plasticise the polymer, and the stickier the powder becomes. A balance needs to be achieved, so for some types of LLDPE it is perhaps better to use lighter ICA (e.g. propane or butane). One can find many instances where more than one ICA is used.^[60,64] The choice to use a mixture can be a trade-off between increasing heat capacity at high levels of heavier ICAs vs trying to reduce stickiness at low levels of ICA and lighter ICAs.

Process constraints. Heavier ICAs such as n-hexane also require higher recycle compressor power than a lighter compound such as cyclopentane for a given mole fraction.^[57] Higher reactor pressures can help heat transfer as the vapour phase is denser and has a higher specific heat per unit volume, and higher pressures also mean that more low boiling (light) ICA can be liquefied in the recycle stream (this means less sticky powder; see above).^[59] It should also not be forgotten that it can be more challenging to run plants using condensed mode in hot climates, and using recycle streams with low dew points can pose certain problems in heat removal under these conditions.^[60] Note that some patents describe the use of 2 stage cooling of the recycle stream (before and after the compressor) as a means of reducing the power consumption of the recycle compressor.^[65,66]

Morphology of the polymer particles. It has been claimed that more spherical particles are easier to fluidise, and so one can tolerate higher levels of ICA.^[62] This is coherent with the discussion above on the stability criteria defined in the Exxon Chemical patents below.^[46,47]

Regardless of what ICA one chooses, liquid levels can be higher for HDPE than for LLDPE since the HDPE will swell less and be less sticky at a given level of ICAs.^[81] It is often important to be able to optimize the amount of heat transfer while keeping the condensate levels constant (in order to smooth operations).^[60] An example of this, taken from reference [60] is shown below. Figure 8 shows the results of a series of simulations of heat removal in an industrial scale FBR. Here we can see the relative amount of heat removed from the reactor in the presence of a mixture of ethylene and nitrogen only (Q_{Base}) versus the amount of heat that can be removed when the nitrogen is replaced by a mixture of ICA with higher heat capacities. The constraints are that the reactor inlet temperature is kept constant at 43°C, reactor temperature at 99°C, and the fraction of liquid in the feed is 17.4 weight percent, regardless of the composition of the mixture. Under these conditions, it appears that one obtains a higher level of heat removal (and thus a higher production rate) with a mixture of pentane and propane, than pentane plus butane. (N.B. as we shall see below, changing the nature of the gas mixture can change more than simply changing the heat removal rate!) The reason one obtains more heat removal with pentane+propane is shown in Table 3 that shows the feed stream compositions for a fixed quantity of liquid in the feed and a fixed inlet temperature. It can be seen here that one does not need nitrogen in the case of

pentane+propane, and the heat capacity of the feed stream is more favorable (under the constraints imposed) than in the case of pentane+butane. Another patent application shows that because n-butane or isobutane do not swell the polymer as much as isopentane, one can use a lot more of either compound and therefore remove more heat.[58]

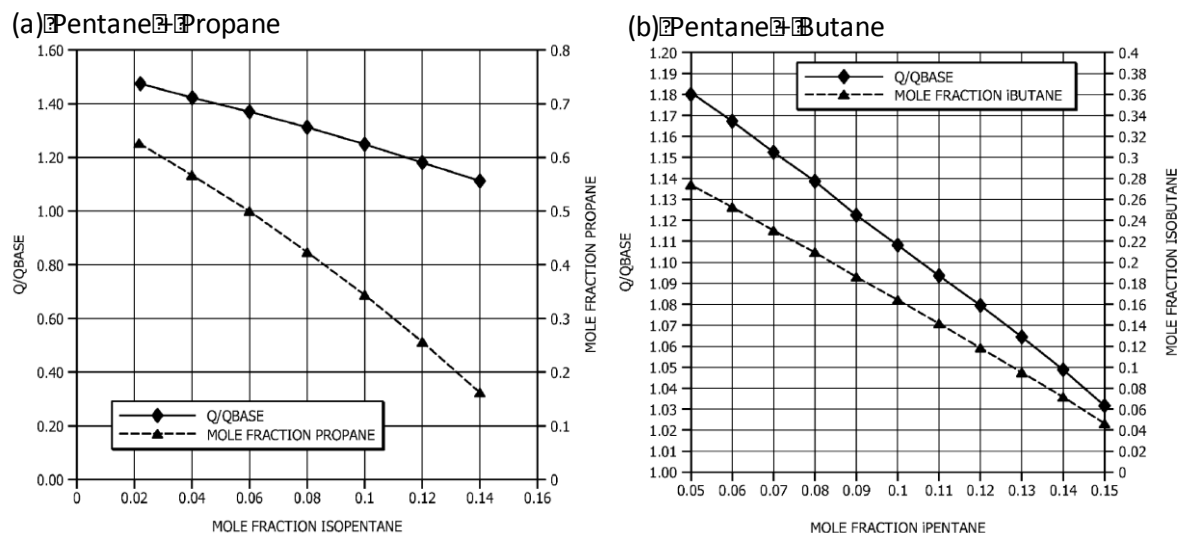


Figure 8. Simulated heat removal capacity from an industrial scale FBR in the presence of a mixture of ICA (Q) relative to the heat removal capacity of the same commercial unit operating with only nitrogen as an inert gas (Q_{Base}). In both cases the condensate level in the reactor inlet is kept constant at 17.4 weight percent liquid at a temperature of 43°C, the reactor temperature at 99°C, total pressure at 21.7 bars (with 7.6 bars of ethylene). The graphs are taken directly from reference [60].

Table 3. Impact of gas feed composition on heat removal at constant (17.4 wt%) condensate level.

Inert/ICA	Mol. Fraction N2	Mol. Fraction Inert/2 nd ICA	Mol. Fraction isoPentane	Heat Removal Rate (MW)	Heat Capacity* (cal·K ⁻¹ ·mol ⁻¹)
Nitrogen	0.48	0	0.17	37.8	8.2
Methane	0	0.492	0.158	37.7	8.6
Ethane	0	0.507	0.143	47.7	10.4
Propane	0	0.628	0.022	55.8	11.6
isoButane	0.325	0.275	0.050	44.7	10.1

*non-ethylene fraction.

Returning to the schema in Figure 7, the gas phase leaving the reactor is compressed, cooled to below the dew point of the mixture, and fed to the bottom of the reactor in order to ensure that the reactor is properly fluidised. No particular specifications are available in the original patents^[12,45] concerning the configuration of the heat exchanger shown in Figure 7, but given the importance of maintaining droplet dispersion, and avoiding liquid pooling and mud formation (see below), one suspects that this type of heat exchanger is likely of vertical design. Note that in these two same patents a

provision is made for the fact that it is also possible to separate the gaseous and liquid parts of the recycle stream, and to feed part of the liquid directly into the be (however these particular inventors clearly stated that they saw little advantage in doing so).

Another interesting point brought up by Jenkins III et al. in the second of these patents^[45] is that the benefit of using condensed mode to cool down a reactor increases as the size of the reactor increases. Given that the amount of heat that must be evacuated from a given reactor increases as the reactor volume increases (supposing a constant yield per unit volume; i.e. a constant space-time yield), the temperature of the gas entering the system must be reduced in direct proportion to the depth of the bed. If we consider first term in the numerator of the right hand side of Equation (2), $\dot{m}_{g,in}c_{pg,in}(T_R - T_{g,in})$ it is clear that the net difference between the inlet and outlet temperatures is important in terms of the amount of sensible heat removal – the actual temperature profile has nothing to do with this. In fact, in the commercial scale reactors described in the examples of references [12] and [45], the authors very clearly state that the reactor bed reaches a constant temperate at a distance of approximately 0.3 metres above the distributor plate in an 11 metre bed. This means that: (i) in most cases seen in these, and the other process patents discussed below, the liquid evaporates very quickly^[67,68,69]; and (b) very shallow beds (e.g. laboratory scale, or pilot scale plants) require feeds that are fairly close to the nominal average bed temperature. In turn, this implies that it is very difficult to run a small reactor in condensing mode with a bed temperature on the same order as that of the full-scale production. At first glance this might not sound like a major problem, especially if the only thing that changes in condensed mode is the amount of energy evacuated from the reactor. However, the inability to run true condensed mode in small-scale (even commercial pilot plant) reactors will have certain important implications in terms of process scale-up. This point will become more apparent when we discuss the thermodynamics of the ICA solubilisation below.

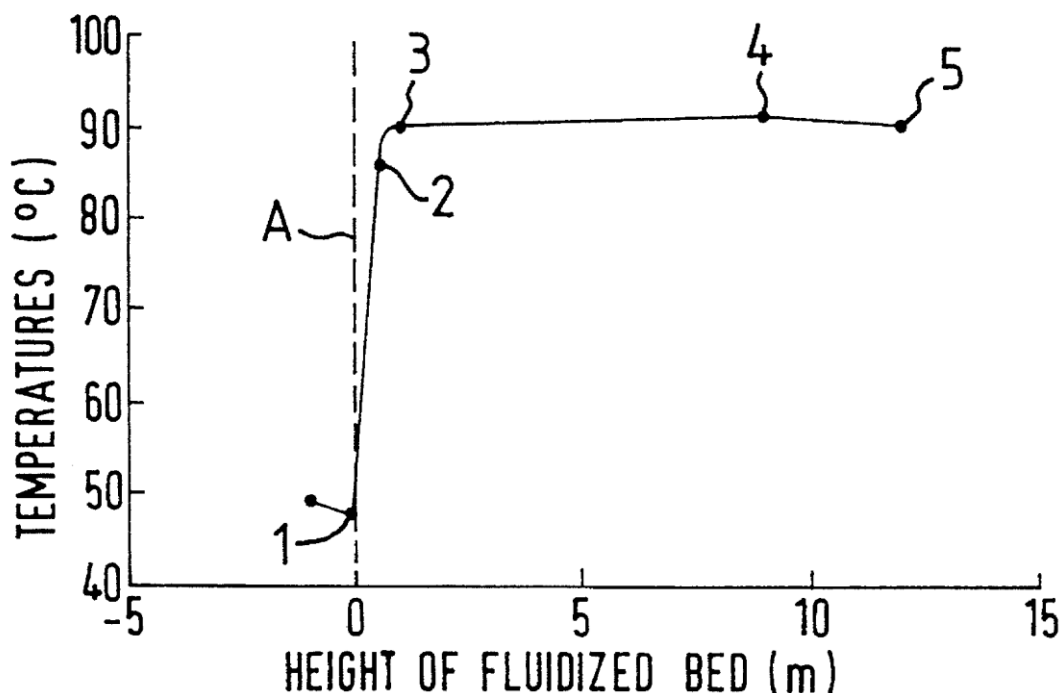


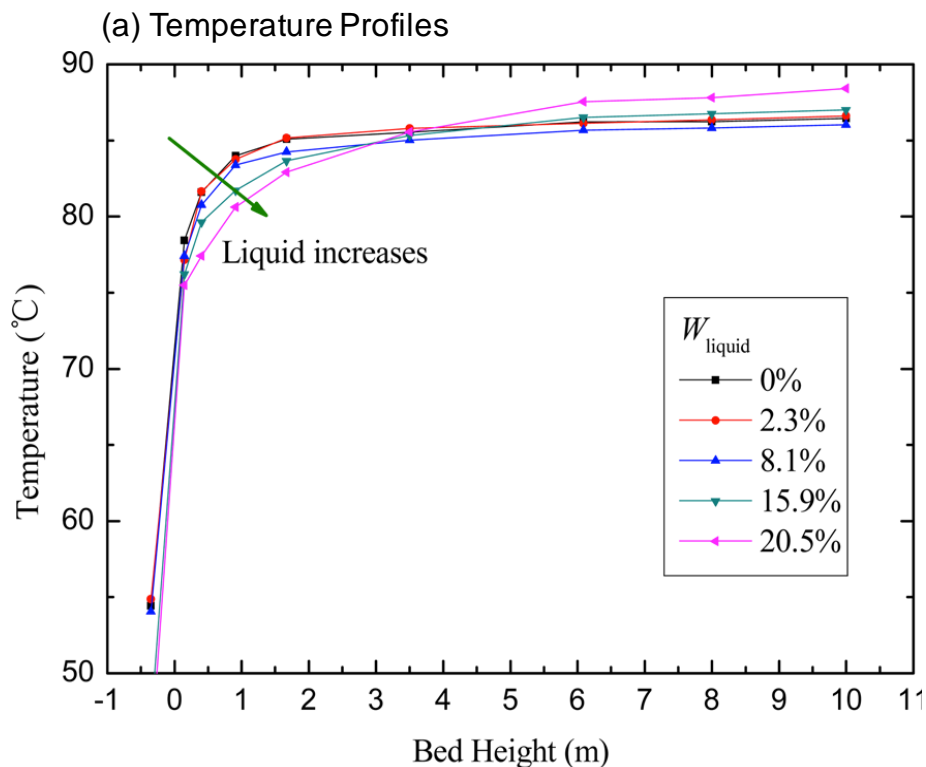
Figure 9. Temperature profile in an FBR with injection of partially liquefied feed.^[67]

Returning to these original UCC patents, according to the inventors^[12,45], one of the principal originalities of these patents with respect to those (and similar) discussed in the previous section lay in the fact that the liquefied components used to cool the reactor are found in the recycle stream that is injected into the reactor to fluidise the bed rather than being sprayed onto – or injected into – the bed. This limitation on the amount of ICA in the recycle stream was imposed to ensure that the liquid in the feed to the reactor was maintained in a suspended condition. In fact, in a related patent^[10] the same inventors point out the importance of maintaining sufficient velocity in the recycle stream so that the liquid droplets are maintained in a suspended state to avoid mud formation (in the recycle and in the reactor), and the accumulation of liquid on or underneath the distributor plate.^[45,58] (This would of course change several years later as technological improvements led to the development of SCM.) The use of baffles or deflectors in the piping near the entry of the recycle stream at the bottom of the reactor to this end, presumably to accelerate the incoming fluid stream and promote atomisation of the liquid, can help with liquid distribution and droplet formation. Based on the importance attached to this information, one could reasonably suspect that the upper limit of liquid in the recycle stream proposed in the original patents is imposed more by a limitation of the available technology (compressors, piping, nozzles, etc.) than by any real thermodynamic constraint.

A later series of patents^[46,47,48], this time from Exxon Chemicals, described how to go beyond the limits of liquid injection (i.e. more than 20% of the feed mass flow rate) that appear to be imposed by the Jenkins III patents discussed above (N.B., “appeared” since Carbide launched a lawsuit against Exxon Chemicals saying their patents did not in fact place an upper limit on the amount of liquid^[70]). Once again, the need for rapid, even distribution of the entering liquid is stressed, as is the need to avoid pooling of liquids below the distributor plate. Certain patent applications even deal with probes that allow one to detect the formation of condensate pooling at this spot.^[71] One of the risks associated with excessive pooling is that if several tonnes of liquid accumulate below the reactor plate, they are not in the recycle stream, and thus not feed into the reactor. This segregation of ICA in the system can lead to a loss of heat transfer capacity and an overheating of the reactor if not detected early enough.

In addition to the risk of pooling of liquid at the bottom of the reactor, another risk associated with high levels of liquid in the feed is that the more liquid one feeds into the reactor, the greater the expansion of the fluid (gas) phase will be upon evaporation, and the more we risk destabilising the bed, ^[72,73] and eventually causing fines to be carried over into the recycle stream. Furthermore, the more ICA one includes in the feed stream, the greater then tendency will be for agglomerates to form (the ICA is, for all intents and purposes, a plasticiser, so the particles will be softer and stickier at higher levels of ICA).^[46] It has been shown that the minimum fluidisation velocity of a wet powder is higher than that of a dry powder, meaning that adding ICA (liquid or not) can directly impact the bed behaviour.^[74] Similarly, if the liquid is not well-dispersed, channeling can be a problem.^[75] Finally, the more liquid we feed to the reactor, the longer it can take for the liquid to heat up and evaporate, and thus the more extended the temperature profile in the bed can become (in other words, Point 3 on Figure 9 will be observed much higher up in the bed). Such large temperature differences could, in

certain cases, lead to poorly defined products.^[47,76,77] As an example, consider the results of a simulation of FBR behaviour in dry (gas-solid, G-S) and condensed mode (gas-liquid-solid, G-S-L) shown in Figure 10.^[72] The simulations show that, as one would expect, the higher the level of liquid in the feed, the less steep the temperature profile in the reactive bed. This can lead to the formation of high molecular weight material that is not seen in the hotter, 2-phase regions of the bed, and thus to a molecular weight distribution (MWD) with a perhaps undesirable high molecular weight (MW) shoulder. Taken to an extreme, this can lead to gel formation, and poor morphology control of the reactive powder.^[77] It has also been observed that under high levels of condensing (i.e. greater than 10 wt% liquid in the reactor feed), it is possible that there is a significant gradient of comonomer in the reactor as well, with comonomer to ethylene ratios being lower at the top of the bed. ^[78]



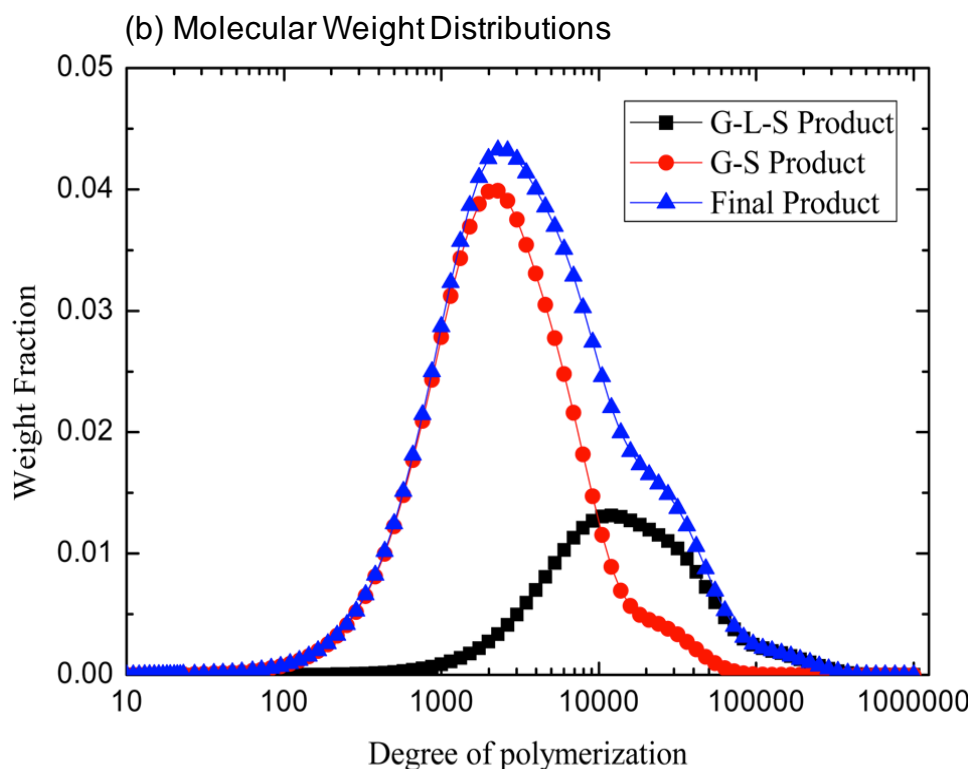


Figure 10. Simulations of (a) Temperature profiles at different levels of liquid in the reactor feed, and (b) molecular weight distributions in the dry part of an FBR (G-S Product), its colder, 3-phase part of the same FBR (G-L-S Product), and of the cumulative MWD. The level of liquid is not specified in the original text. Reprinted with permission from Zhou et al., *Ind. Eng. Chem. Res.* 2013, 52, 4455–4464. Copyright 2013, American Chemical Society.^[72]

A variety of other points about using condensed mode cooling include:

Fines reduction. The need to be sure to avoid presence of fines in the recycle stream is also discussed in patents. There are clearly multiple reasons for this, but the most important will be: (1) to stop fine particles, and in particular particles that are still polymerising, from entering (the very expensive) recycle compressor; and (2) to avoid forming mud from a mixture of fine particles and liquid components. The first reason obviously applies to all plants, whereas the second is specific to condensed mode. In references [12] and [45], the authors state that they use deflectors at the entrance to recycle heat exchanger to knock out any fines entrained in the recycle stream. An earlier patent for Standard Oil talks about separating out the fine particles (HSBR process) and feeding them directly back into the bed to prevent problems with lumps and sludge^[79]. One can see in Figure 4 that even in very early processes a cyclone was included at the outlet to the FBR to knock out fines as well.^[34] This last method is still used in the Innovene G process^[13], and referred to as Clean Loop Technology^[80]. The choice about whether or not to use a cyclone will depend on a combination of economic and technical factors that are beyond the scope of this text.

Injecting an ICA (or mixture of ICA) into a reactor appears to help reduce the level of fines in the reactor in condensed ^[69,70,81,82,83] or dry ^[84] modes. It is entirely possible that this is due to the softening of the polymer particles due to the plasticising effect of the

ICA.^[81] It is well known that one means of reducing fines in a (dry mode) HDPE process is to increase the temperature to soften the particles, so it is reasonable to suspect that softening via ICA addition will yield a similar effect. It was also pointed in reference [84] that while injecting vapour phase hexane into the reactor lead to a decrease in the level of fines, it also corresponded to an increase in the average particle size (we will return to this point below). It should also be pointed out that in patents where fines reductions are part of the reason to use condensed mode, an accompanying reduction in sheeting seems to follow.^[83] In part this improvement can be associated with the reduction of static electricity in condensed mode of operation.^[85]

Reference [45] states that tolerance for a small level of fines in the recycle stream can reduce capital costs like investing in cyclones, but when operating in condensing mode this is more problematic because the fines can create mud in the recycle stream. Note that this need to avoid fines in condensed mode also places a limitation on the velocity of the fluid stream *in the reactor* since high gas velocities correspond to high carry-over of fine particles (typically one finds between 0.1 and 1 wt% particles in the exit gas stream). In addition, Jenkins II et al. ^[45] point out that when transitioning between CM and DM/SDM, it is very important to do so quickly. In fact, it appears that if just small quantities of liquid are present in the recycle stream (<2 wt%), mud formation will be a problem. However, different ways of reacting this problem exist. On the other hand, the use of a cyclone at the reactor outlet allows one to remove a significant fraction of the fines that might leave the reactor, thereby allowing one more leeway in terms of liquid levels that can be tolerated in the recycle stream (albeit with the increased capital investment of installing the cyclone).

Liquid carry over. Another technical problem to be aware of is that at high levels of liquids in the reactor, it is possible that a significant amount of ICA (even liquid ICA) can be carried over into the discharge system.^[86,87] This can cause rapid expansion in the discharge vessels, leading to a loss of withdraw and degassing efficiency, and even mud formation and plugging of process lines.^[88] While not explicitly mentioned in the cited patents, this means that retrofitting existing plants to run in condensed mode requires one to take into consideration certain design aspects relative to the discharge system of the reactor.

Flooding and overcooling. In the event that the reaction slows down (e.g. purity problems, temperature control, etc.), then if the heat removal capacity of the reactor exceeds the actual rate of production of energy the ICA might not totally evaporate, and one can experience rapid flooding or frothing of the reactor.^[88,89] Even if the reactor does not flood, accumulation of significant levels of cold liquid at the bottom of the reactor can lead to uneven temperature profiles, which, as mentioned above can lead to problems related to product quality.

Production vs Catalyst mileage. One objective of condensed mode is to increase space time yields (production rate). In some instance this can lead to a reduction in the average residence time^[90] (if not the residence time distribution) and therefore adversely influence the polymer properties.^[77] The down side of the uptick in production is the loss of catalyst mileage, and the risk of catalyst residue in the final product as a result. ^[46] On the other hand, for certain catalyst systems this appears to be rectifiable via a choice of ICA. In one patent to Univation Technologies LLC, the

inventors claimed that switching from isopentane to isohexane allowed them to increase the bulk density of PE particles by a factor of almost 17%.^[91] Denser particles meant the residence time increased.

3.3 A Brief Look at some Technological Issues

In the original condensed mode patents to UCC^[12,45], the designs focused on injecting the liquid into the bottom of the reactor, and although the authors mention that injecting liquid into the bed is possible, they clearly state in their earlier patents that this is not an attractive solution (for them). These patents, and others^[62] show that the partially liquefied feed stream comes through the bottom of the reactor and hits a deflector plate. The idea being that the force of impact will atomise the liquid droplets present in the incoming stream, making them easier to disperse and facilitating the droplet evaporation step since smaller droplets vaporise more quickly.^[92] In more refined set-ups the feed injection nozzle will be important. A patent^[10] awarded to Union Carbide clearly shows the technology such as the feed nozzle, distributor plate, and type of flow deflectors installed in the reactor bottom are essential (at the time this current paper is being written, this patent by Rhee et al. has been cited over 120 times by other patents, so one is led to suspect it is quite relevant). It has been pointed out that it is very important to consider the technology used at the bottom of the reactor (i.e. where the liquid/vapour feed is injected), as they point out that certain types of inlets are not suitable for condensed mode cooling.^[10,9] In particular, the conical or cap-type distributor plates typically used for DM/SDM (and undoubtedly the technology used prior to reference [12]) cannot stop the liquid injected into the bottom of the reactor from leaking down below the distributor plate. On the other hand, injectors that were often used for condensed mode, where the incoming vapour/liquid stream rapidly expanded due to droplet vaporisation were designed to account for the expansion, and allow excessive build-up of polymer powder in DM/SDM. In this patent,^[10,9] the authors stress (among other things) the significance of the geometry and other design parameters of the deflector. This annular deflector, shown in Figure 11, divides the incoming flow into two major portions. The first (33 in the diagram) is the central flow that is intended to entrain the liquid droplets upward through the protective screen (27), and out the holes (29) in the distributor plate (28) protected by the angle caps (36). The secondary flow (33a) is intended to prevent pooling of condensed liquid at the bottom of the inlet section. Of course, this is not the only type of flow deflector design possible. The plate from which the annulus is formed can be inclined and/or conical^[93], or even be similar to the one shown in Figure 11, with a conical distributor to help even the flow out of the central annulus.

condensable material in the bed. This will of course be easier and more rapid if the gas and liquid streams are injected separately.^[101]

Other injection modes have been proposed as well. For instance, some Union Carbide patents proposed that instead of spraying droplets into the bed, the liquid phase could be separated out and fed to the reactor in different ways: (1) conventionally near the bottom of the reactor, above or below the distributor plate; and/or (2) through nozzles situated at different heights in the bed, and at the very top of the bed (in the conical disengagement section) and allowed to flow down the wall of the reactor.^[96,102] The authors claim that spraying at least a portion of liquefied alkanes onto the top of the bed helps reduce carry-over of fines. Similarly, Basell also patented a process (with no patent examples) that claims that liquid can be sprayed on to the top of the bed.^[103] However, one suspects that this will be at the price of a reduced efficiency in terms of heat removal per kg of ICA injected. Chinh et al.^[13,104] clearly state that the most efficient operation is obtained when the cold liquid (injected separately and above the distributor plate in this patent) is injected at a height close to that where the gas phase has reached its steady value (c.f. point 3 in Figure 9). Nevertheless, these points do not take into consideration the volume of the bed, and a much later patent from Ineos discusses different injection schemes FBRs with volumes over 250 m³.^[105] Experience combined with computation fluid dynamics (CFD) simulations suggest that in reactor of this size (and larger), one can get both axial and radial temperature gradients. Thus, as in the case of the Union Carbide patents cited above in this paragraph, they suggest in SCM, injecting liquid at different levels in the reactor to help avoid hot spots and temperature inhomogeneities that can lead to loss of bed stability. While it is difficult to say from the patent exactly how the liquid is distributed in the bed, it appears that at least half of the liquefied ICA can be injected at heights going up to $\frac{3}{4}$ of the bed depth. It is claimed that this distribution of fluid keeps a more even temperature, and better fluidisation. The inventors also claim that it is easier to use higher gas velocities in this case. While they do not say why it is possible that the more even distribution of vaporising fluid throughout the bed gives one a more controlled expansion.

In all of the operation modes where liquid (or partially liquefied) streams are injected into the reactor above the distributor plate, it is necessary to use specially designed nozzles.^[10,13,46,67,68,94,95,106] When injecting a (partially) liquefied stream, one of the issues to avoid flooding, frothing and return of the liquid back down the feed pipe, especially as the amount of liquid increases.^[10,107,108] While capped pipes are fine for dry mode operation, nozzles are needed for condensed mode – so if one needs to switch back and forth between different operating modes it is necessary to design the reactor accordingly. Different applications require different nozzles, but one thing that appears to be important is the need to disperse the liquid in the form of fine droplets.^[109,110] If the injected liquid does not atomise immediately it is possible to form agglomerates – basically lumps of polyethylene “mud” in the reactor.^[13,67,111,112] This can easily lead to the destabilisation of the bed, and plugging of the product disengagement lines. Unfortunately, the majority of the open scientific literature in this field appears to be dedicated to studying how best to wet particles in an FCC solid-gas bed^[113], which is pretty much the opposite of what we want to do here. What is clear from the open patent literature is that the number and positioning of the nozzles in the bed, their depth of penetration and orientation, the velocity and direction of the liquid stream will all be very important parameters in obtaining optimal liquid injection conditions.^[67,68,94,95,114]

For instance, in several patents to B.P. Chemicals [13,67,68,94,115] present different nozzle designs, two of which are shown in Figure 12. There are generally several nozzles spaced around the reactor wall at a given height (in the reference [13] the authors claim to use 2 to 3 nozzles per 10 square metres of bed section.). The nozzle on the left of Figure 12 typically uses make-up nitrogen or ethylene to force the liquid stream through a series of jet openings, thereby atomising the liquid phase. These droplets are most likely on the order of 10 to 150 microns as droplets in this size range will evaporate sufficiently quickly.^[92,112,116,117] It turns out that the problem with these nozzles is that they will plug when the reactor is run in dry mode, so more sophisticated designs, such as the other two designs shown in Figure 12.

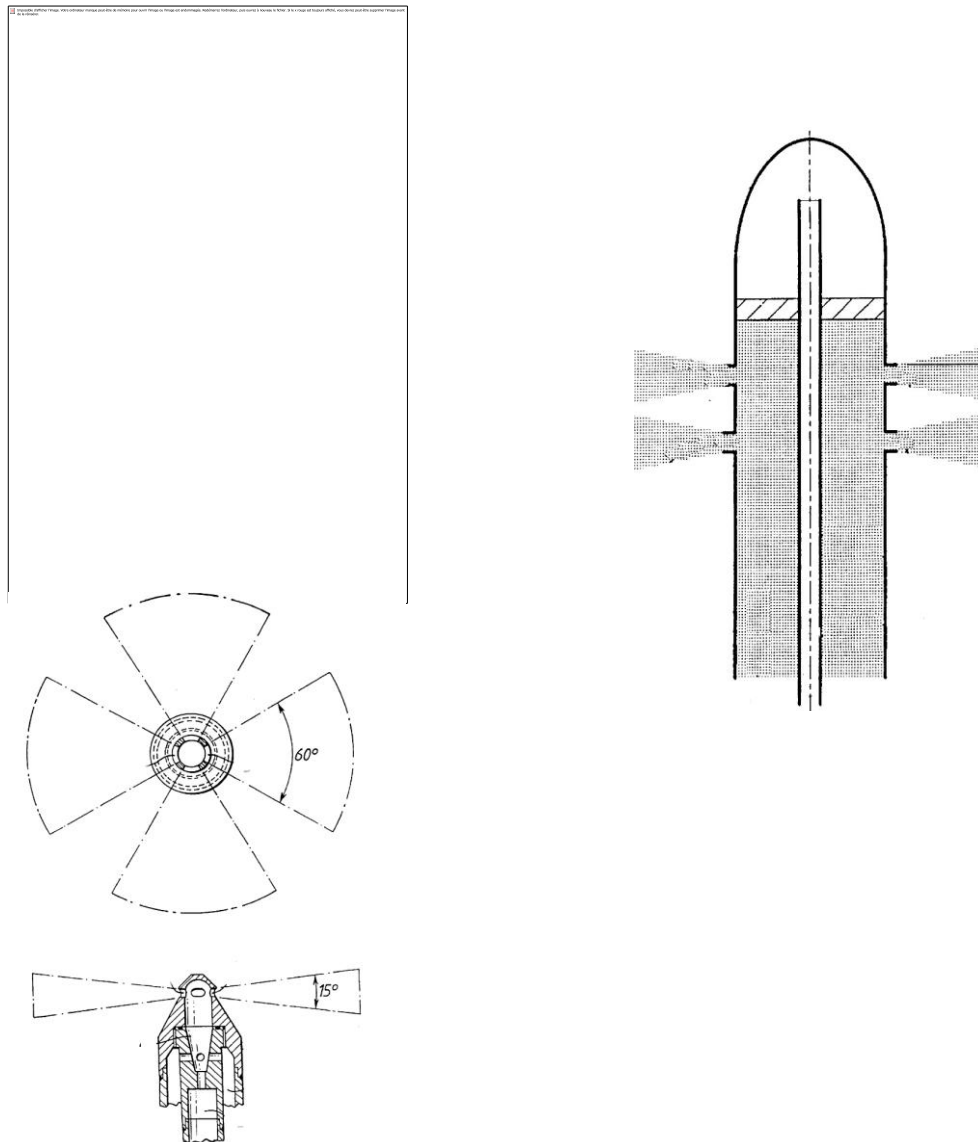


Figure 12. Different nozzle designs for the injection of liquid streams into an FBR at a spot above the distributor plate. Left, a nozzle for atomising a liquid/gas stream. [13,67] Centre^[107] and right^[118], additional nozzle configurations to prevent plugging problems when operating in dry mode.

3.4 FBR Stability and Monitoring in Condensed and Super Dry Modes

To quote the authors of reference [46]:

“The control of a fluidized bed therefore has to be exercised to reduce chunking and sheeting and to prevent bed collapse or a need to terminate the reaction and shut down the reactor. This is the reason why commercial scale reactors are designed to operate well within proven stable operating zones, and why the reactors are used in a carefully circumscribed fashion.”

And

“... changes in the process of one or more of the measured values lead to consequential changes elsewhere. In the design of plant the optimization of capacity depends on the most restricting element in the overall design.”

These points, coupled with the fact that fluidisation is a very complex issue, very closely linked to the reactor size and shape, mean that industrial engineers are loath to do “experiments” on commercial-scale FBR, and that things that impact smooth operation are learned incrementally from small changes in operating conditions over time. In this sense, and to avoid the problems of stability, chunking and sheeting mentioned above, the authors reference [46] (and subsequent patents) used readily identifiable parameters for initial efforts to avoid problems. Thus, in these initial patents on super-condensed mode, the authors used easily measured parameters linked to pressure drop in the bed to set operational limits. One specification they proposed was to maintain a ratio of the fluidised bulk density (FBD) to the settled bulk density (SBD) higher than 0.59. The FBD can be directly linked to the pressure drop in the bed, and can be measured any number of ways at different levels in the reactor.^[121] Since the pressure drop across the bed is close to the bed weight divided by the cross section of the reactor, the pressure drop divided by the bed height gives a good measure of the FBD (and presumably the SBD is simply the bulk density of the powder in question). Events such as the rapid or excessive expansion of the of the emulsion phase will cause the FBD to drop (possibly due to changes in the bubble behaviour in the bed^[47]), whereas agglomeration can cause the SBD to increase. This limit of 0.59 thus appears to a kind of empirical guideline representing an acceptable trade-off between the 2 opposing phenomena. An interesting point is that the authors explicitly state that the FBD/SBD ratio is not necessarily linked to the liquid level (i.e. even in dry mode operation the reactor will run into problems if the ratio in question is less than 0.59). The authors claim if one keeps the FBD/SBD ratio within an acceptable range, then it is possible to have high (i.e. 20 wt% or more) levels of condensed material in the recycle stream. They show examples in the patent with an industrial scale FBR running at 38.6 wt% condensed C6 hydrocarbons in the recycle.

Of course, maintaining good bed stability is more complicated than simply keeping the $FBD/SBD > 0.59$, since things like particle morphology and stickiness, superficial velocity etc., will also be important. Furthermore, one must also consider constraints due to product removal from the reactor. Changes in morphology, SBD and fluidity etc. can pose certain challenges to product discharge, and if one cannot remove the product fast enough the only way to maintain good bed stability and depth is by reducing the

catalyst flow rate (and thus limiting the gain in production due to the use of condensed cooling). Thus reference [47] extends the analysis of the patent in reference [46] to include more factors in defining regions of stable bed operation than simply $FBD/SBD > 0.59$. Here, the authors define a bulk density function:

$$Z = \frac{(FBD - \rho_g)/SBD}{(\rho_{pol} - \rho_g)/\rho_{pol}}$$

where ρ_{pol} is the density of the polymer and ρ_g is the density of the gas phase. They then developed a chart of acceptable values of Z as a function of the log of the average particle Reynolds number (nature of gas phase flow) and of the Archimedes number (buoyancy versus viscous forces). This provides a more refined safe operating envelop than FBD/SBD ratio, but the basic idea is the same: one needs to account for changes in both gas phase and particle phase properties due to the presence of ICA in order to ensure stable operation. Other patents go on to extend references [45] and [46] to metallocene catalysts and to comonomers heavier than hexene^[48,119,120]; yet others further refine the numerical criteria for maintaining stable bed operation, including keeping the comonomer content to a minimum.^[119,120] Other patents propose similar schemes based on a difference between the upper and lower FBD to define a stable operating window as a function of the temperature profile.^[64]

It was mentioned above that keeping the dew point of the recycle stream close to the reactor temperature allows one to remove more heat at a fixed recycle temperature. However, the problem is that when one is dealing with copolymers, especially with 1-hexene or 1-octene LLPDE in particular, the closer the dew point of the reactor stream is to the reactor temperature, the stickier the polymer will be. Ditto for high hydrogen levels. These authors thus propose that the temperature difference between the dew point of the feed and the reactor difference be at least 5, or even 10°C, and that the ratio of the mole fraction of comonomer plus hydrogen to that of ethylene be less than 0.1. They also point out that this is easier to do with the appropriate metallocenes if they have good sensitivity to comonomer and to hydrogen.

Later on, process control schemes used measurements of the FBD at different spots in the bed to detect local defluidisation and channeling, and used different indices based on these measurements to control (reduce) the levels of condensable material in the bed under critical conditions.^[121] Other patents point to using the mode of fluidisation to help with bed stability at high levels of ICAs.^[62] In reference [62], the authors propose pass run the reactor under conditions of turbulent (rather than bubbling) fluidisation, coupled with keeping the ratio $FBD/SBD > 0.59$ as noted above. The transition between the two regimes depends on both the superficial gas velocity and the density of the fluid, so the more condensed material one has in the recycle stream, the lower the superficial velocity required to maintain turbulent conditions is. However, while pressure drop measurements are simple to obtain and can probably provide some guide as to the bed stability, it is known that pressure measurement are somewhat insensitive to the onset of defluidisation (often caused by the agglomeration of particles)^[122], as so other methods were developed to control bed stability.

Furthermore, once particles begin to agglomerate in an FBR, it is almost always necessary to shut the reactor down to take care of the problem. Among the many issues

that lead to agglomeration, chunking, and loss of fluidisation, one of the key problems associated with using ICA in an FBR is that of polymer stickiness. Obviously the higher the temperature of a polymer is, and the more plastifier it has absorbed, the stickier it will be. As already mentioned heavier components such as 1-hexene or n-hexane are more soluble in PE at a given temperature than lighter components such as n-butane or propylene. Thus the composition of the gas phase will be at least as important as the temperature in this sense. Quantifying stickiness is a tricky problem, but different approaches have been proposed in the patent literature. In a patent to Univation Technologies^[53], the authors defined a critical temperature beyond which the polymer becomes too sticky for safe reactor operation, as that temperature where 15% of the crystalline fraction of the polymer has melted for a ZN catalysed polymerization. This limit can be as high as 30-40% for a metallocene because it has a narrower composition distribution^[123,124].

The authors of reference [53] also proposed a method of quantifying stickiness using a thermal analysis method. The sticking temperature of a dry powder (T_{DS}) can be determined empirically by fluidising a powder of interest in the presence of nitrogen alone. No other processes gases are present in order to eliminate any swelling or softening of the polymer. The fluidisation is begun at a temperature of 40°C, and the vessel temperature is increased at a rate of about 2°C per hour. The temperature is raised until wall fouling or agglomeration is observed (or if the pressure drop measurement becomes too noisy). Then differential scanning calorimetry (DSC) thermograms are obtained for the dry powder, and the powder soaked in an ICA. The melting point depression (ΔT_m) is defined as the difference between the two melting points. Finally the critical reactor temperature (i.e. the maximum allowable temperature) was defined as $T_c = T_{DS} - \Delta T_m$. The reactor temperature in the presence of an ICA must be lower than this critical temperature for safe reactor operation. It is claimed that typical values for ΔT_m in LLDPE plants can be up to 22°C (depending on the amount of ICA, and the type of polymer and of catalyst).

The concept can be seen from the data in Figure 13, which shows 2 different (experiment) thermograms of an HDPE powder.¹²⁵ The blue curve is for dried powder, and the black one for the same HDPE powder, but with the sample capsule containing 20 wt% (with respect to polymer) of n-hexane. We have no access to the value of T_{DS} as defined in the aforementioned patent, so in this case we will use the the temperature at which 15% of the crystalline material melted as the sticking point. For the dry powder this is 100°C (determined from the DSC software). The ΔT_m in this case is 7.4°C, meaning that $T_c = 92.6^\circ\text{C}$ in the presence of the ICA. Thus, the dry HDPE production could take place at 90°C, but if polymerisation in the presence of hexane took place at this temperature one might experience problems as it turns out that the sticking temperature (same definition) of the HDPE in the presence of hexane is 86°C.

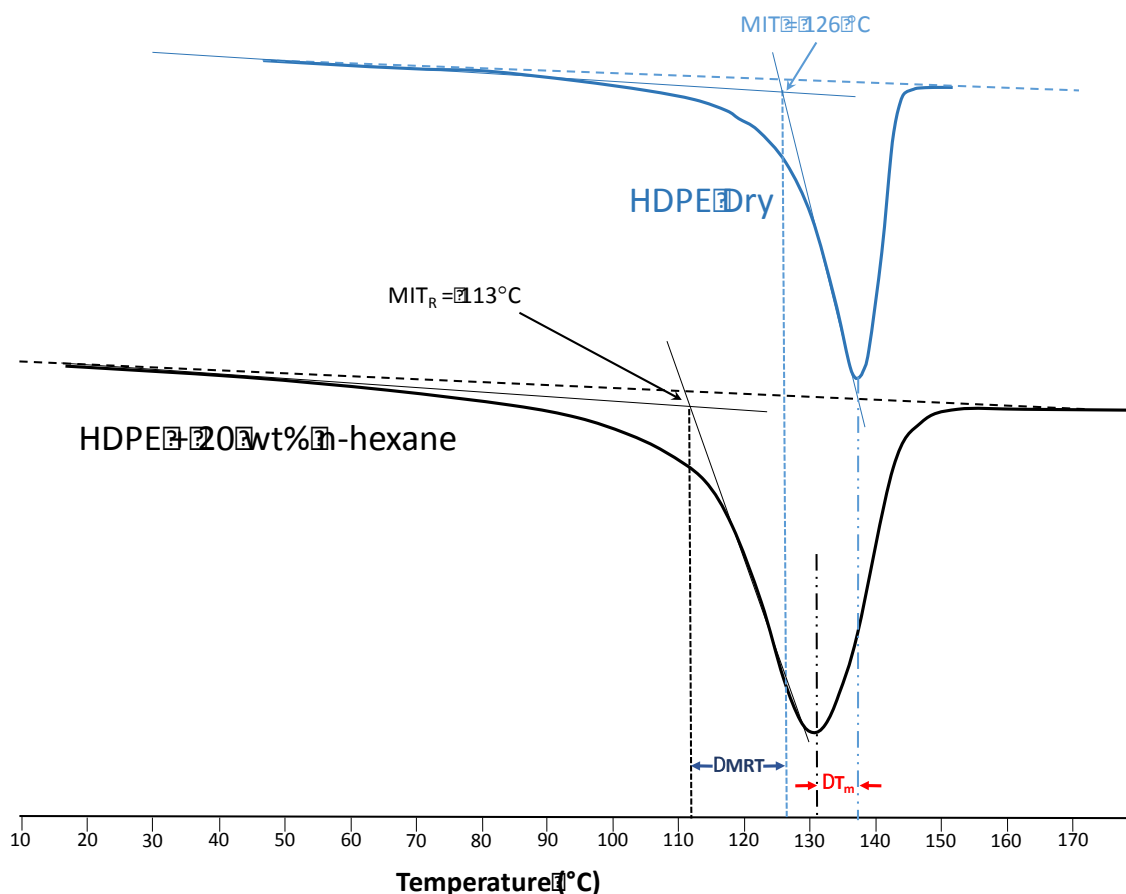


Figure 13. DSC thermograms (first melt) of an HDPE sample (blue curve), and of the same HDPE mixed with 20 wt% n-hexane in the analysis capsule. Here ΔMRT is the difference between the measured melt onset temperatures, and ΔT_m the difference between the peak melting temperatures. Unpublished data. Polymerisation conditions: 7 bars ethylene, 80°C, 0 bars hydrogen, commercial Ziegler Natta catalyst.

Later patents used a similar approach to defining stickiness, but changed the nomenclature and definitions. The underlying idea was similar, but relied on (first melt) DSC measurements to define a stickiness parameter that reflects a change in the melting behaviour in CM with respect to DM.^[123,126,127,128] The idea and with an eye to applying this on-line as a stand-alone method,^[123,126] or in conjunction with more sophisticated expensive acoustic methods.^[127,128] In this approach, the authors used the melt initiation temperature (MIT; also called the melt onset temperature) as a characteristic temperature of the onset of melting.

The MIT of a polymer will be a function of the polymer properties (degree of crystallinity, branching, MWD), and gas phase temperature and composition. As shown in Figure 13, the MIT is the temperature at which rapid melting of the polymer begins (this value is generally provided by the software of most DSC). The MIT is defined as the value for polymer made in the absence of ICA (blue curve in Figure 13), and the reduced melt initiation temperature (MIT_R) is defined as the same temperature in the presence of an ICA (or mixture of ICA), and that reflects a reduction in the onset of melting due to change in the reaction conditions. If one can identify a value for MIT_R, this can be used

as a reference value for controlling the reactor temperature to avoid catastrophic agglomeration or fouling in the reactor. The authors of the patents defined the difference between the onset of melting and the maximum allowable reactor temperature, ΔMIT , as the stickiness control parameter in the following manner:

$$\Delta MIT = T_R - MIT_R$$

In other words, if one knew the value MIT_R , and could find a value for ΔMIT , then it would be possible to control the bed temperature T_R in order to avoid problems of sticking.^[129] One way to find MIT_R discussed in the patents is to use equations of state to find the melting point depression of the dry powder in the presence of a solvent, $D = \Delta T_m$, and applying this same depression to the MIT.^[126] In this case, we would assume that $MIT_R = MIT - D = MIT - \Delta T_m$. In principle, it should be possible to generate correlations such as these for the MIT as a function of density, melt index and other relevant properties.^[130]

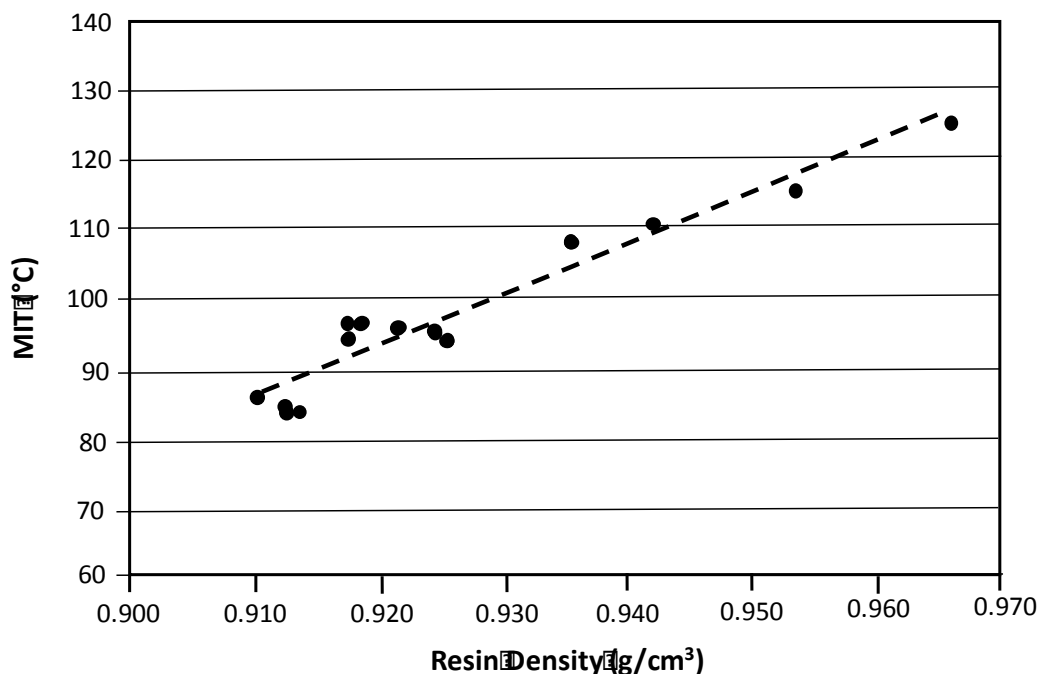


Figure 14. MIT (dry) of an LLDPE as a function of resin density. Melt index and other properties not specified.^[130]

However, as pointed out in these patents, and as one can see from Figure 13, even if one had a very good estimate for the melting point depression, $D = \Delta T_m$, MIT_R would be overestimated by this method as $\Delta MIT > \Delta T_m$ for this particular polymer. In reality the gas phase of a commercial reactor can contain different concentrations of several compounds, all of which will impact the melting behaviour of a powder in complex ways (see section 4 below), so it is probably illusory to imagine that one could calculate ΔMIT accurately for a complex mixture of penetrants (assuming that MIT values are available!). Thus more physically representative ways of controlling stable bed operation were sought.

As mentioned above, piloting reactor operation using FBD/SBD based on pressure drop measures, it is likely that they can be successful in a number of situations. However, the complexity of the phenomena related to polymer swelling in terms of the impact of polymer properties and gas composition (see below), the impact of flow patterns, grade changes and normal process fluctuations, it would be preferable to have a method that allows one to actually predict (as opposed to prevent) operational problems linked stickiness, sheeting, and loss of fluidisation. Having a wide range of tabulated ΔMIT values would help, but unless these can be measured on-line this method is probably also limited given the complexity of what actually determines its value. Producers therefore sought other methods, and since the early 2000s the use of acoustic spectroscopy has been discussed as a means of adding predictive capacity to the monitoring of agglomeration and flow in FBRs for the production of PE [72,127,128,129,131,132,133,134,135,136,137] (alone, and in combination with static probes^[138]).

A discussion of the underlying theory behind acoustic emission spectroscopy (AE) is beyond the scope of the current article, but basically acoustic sensors can be placed at different heights on the outside of the FBR and used to follow the ultrasonic emissions of particle-wall and particle-particle collisions. The simplest way to put this is that the noise from the reactor becomes attenuated as the polymer softens.^[127] For example, particles banging into a clean steel wall make more noise than a powder banging into a wall covered in polymer. As an example, a pilot plant shown schematically in Figure 15 was used to collect the data in Figure 16. Figure 16 shows a compilation of measurements presented in a Univation patent where a pilot plant reactor was driven to the sticking limit purposefully.^[127] At the start of data acquisition the pilot plant is operating at steady state and making LLDPE with a density of 0.917 g/cm³. A series of potentially destabilising changes are imposed on the reactor, with additional hexene being added after approximately 24 hours of steady state operation. After 47 hours, 6.8 mol % isopentane (this is still “super dry” mode) is added as an ICA. This initially provided good heat transfer control and less sticking (higher AE in both parts of the bed). Then at 59 hours the superficial velocity is dropped. This led to hotter particles, and more sticking (the AE drops). Note that although AE changes to reflect the changing stickiness conditions, the FBD remains impervious to any of these small changes. After 80 hours a slowly increasing ramp of 2.8°C/h was imposed on the reactor set-point. Here, the AE drops very rapidly and shows a strong change in the stickiness of the particles several hours before the FBD measurements reveal the problem. Additionally, if one considers the skin temperature measurements, they are only slightly more responsive under these conditions than the FBD.

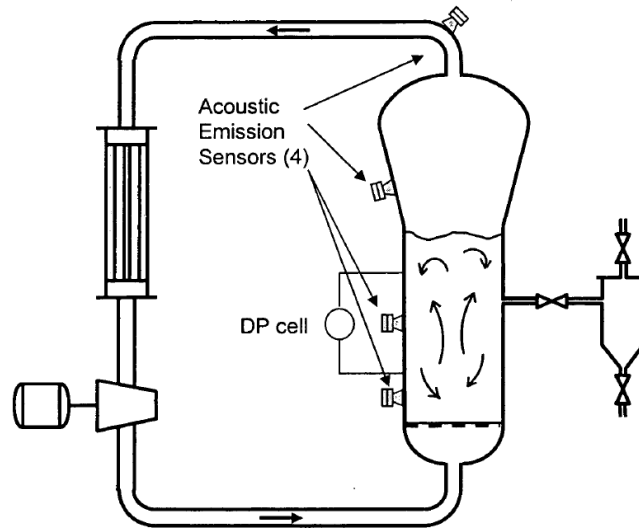


Figure 15. Pilot scale FBR with 4 acoustic sensors to collect AE spectral data, and two pressure cells to measure the FBD. Data in Figure 16 were collected using the 2 lower AS sensors. [127]

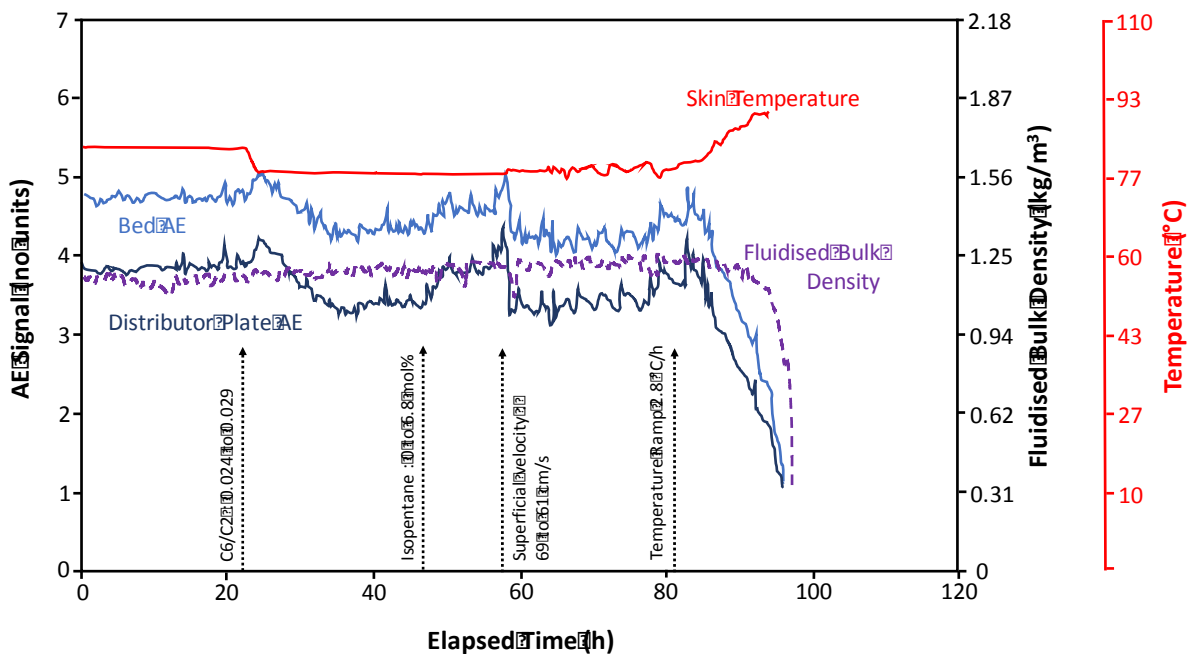


Figure 16. Results of a pilot plant run for LLDPE. At approximately 21 hours the density is decreased from 0.917 to 0.911 g/cm³ by changing the hexene/ethylene ratio. At 44h, isopentane is introduced. At 58 hours the superficial velocity is dropped and at just over 80h the set-point temperature is ramped up at 2.8°C/h. Adapted from reference [127].

Despite the interest of this type of approach, and as pointed out by the authors, the data in Figure 16, while quite useful and informative, do not allow one to predict at what temperature the critical stickiness will occur, nor what the value of ΔMIT would be. One approach to find this stickiness control parameter was presented in reference [129], and is illustrated in Figure 17. Here we see a large data set showing the acoustic signals

obtained from a commercial scale FBR in which a range of products with different densities (ρ) and reactor conditions were produced. This graph shows the acoustic signal for Very Low Density PE (VLDPE) and LLDPE products. As mentioned above, as the polymer becomes stickier (i.e. ΔMIT increases), the lower the AE is. Just so long as the AE remains at 1.5V, one can consider that we are operating in safe territory. However, beyond a certain point, and depending on the physical properties of the polymer in question, operating in condensed mode can lead to a decrease in the AE, and thus an increase in the risk of stickiness. Experience will allow one to define a limiting AE, below which one does not want to go. This corresponds to a maximum ΔMIT . If reactor temperature exceeds alarm point temperature, then we risk running into problems of agglomeration. If we know this value, we can pilot the reactor temperature in such a way that we remain below this critical value. Once again, this is a method that requires a large data base for a range of materials, but once that has been established, one can use the AE to pilot the reactor and, in theory at least, avoid problems requiring reactor shut down.^[129,138] Note also that it is not entirely clear how this method would be applied during transient phases of operation such as grade transitions, when the reactor contains a mixture of different products.

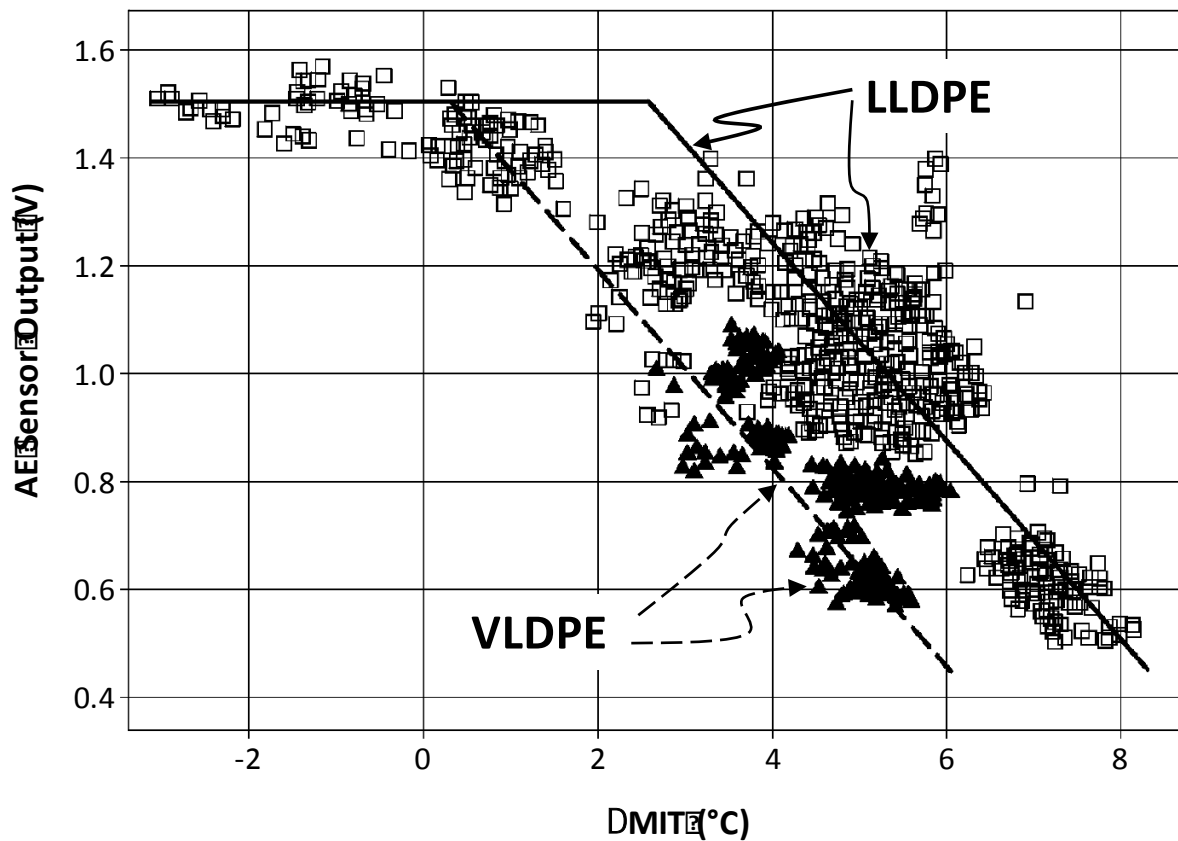


Figure 17. Acoustic sensor output (AE, in volts) as a function of ΔMIT for VLDPE ($\rho < 0.9165$; dashed line, closed symbols) and LLDPE ($\rho > 0.9165$; solid line, open symbols). Adapted from US Patent 8,383,739.^[129]

4 Impact of ICA on Properties, Rate and Other Important Issues

4.1 Thermodynamics: solubility and diffusivity effects

We have seen that the addition of an ICA, liquefied or not, increases the heat removal capacity of a reactor, thereby allowing one to polymerize more quickly. The discussion above also shows that, especially in the earlier stages of the exploitation of condensed mode cooling, most of the focus was on maintaining bed stability in the face of ever-increasing amounts of liquids in the recycle loop. However, the impact of alkanes (or alkenes for that matter) is more complex than simply increasing the heat removal rate from the reaction. It is well-known that the thermodynamics of penetrant-polymer systems can be quite complex. Penetrants can plasticize the amorphous fraction of the polymer, leading to changes in the physical and mechanical properties of the parties in the reactor. In addition, non-ideal swelling in multicomponent systems can lead to complex interactions, and often make the use of simplified models such as Henry's Law quite inaccurate.

In fact it is reasonably well-accepted now that the ICA can have an impact on the solubility of other species in the polymer layer surrounding the active sites on the particle, this is clearly the case. It was shown as early as 1957 that when 2 penetrants are solubilised in polyethylene, the heavier one enhances the solubility of the lighter one.^[139,140] If one considers the simplified case of a polymer and two penetrants, for instance ethylene and an ICA, the higher the concentration of the ICA, the higher the ethylene concentration will be in the amorphous fraction of the polyethylene.^[141,142,143,144,145,146,147,148,149,150,151,152] Obviously this should have an impact on a certain number of values, in particular the molecular weight distribution and the rate of polymerisation. In addition, while it is more difficult to quantify, one could also say that the quantity and type of ICA could also influence the crystalline structure, level of amorphous material, and thus further impact the solubility of monomer(s).

A detailed review of the complex interactions between multiple penetrants and different polyolefins is outside of the scope of the current paper, but it is useful to consider a rapid overview of the state-of-the-art in this area as it is clearly going to be very important in SDM, CM, and SCM operation. One of the earliest papers to look the impact of sorption effects in olefin polymerisation was Hutchinson and Ray.^[153] These authors reviewed some of the earlier literature and showed that simple thermodynamic expressions like Henry's law are valid for light penetrants (e.g. methane, ethylene) at low to moderate pressures, but that heavier penetrants and other conditions that lead to the swelling and/or plasticisation of the amorphous phase of the polymer. They developed a rather straightforward model to predict the conditions under which a heavier penetrant (e.g. an ICA) will enhance the sorption of a lighter component. Among the many important points raised in this article, the authors demonstrated that if one accounts for cosolubility effects, this has a profound impact on the estimate of kinetic constants such as the propagation rate constant, and the reactivity ratios in the case of a copolymerisation.

Several years later, variations of different equations of state (EoS) have been explored to model solubility in ternary systems, in particular Statistical Associating Fluid Theory for potentials of Variable Range (SAFT-VR)^[154,155], Perturbed-Chain Statistical Associating

Fluid Theory (PC-SAFT) EoS^[144], simplified versions of these 2 models,^[156] and the Sanchez-Lacombe EoS (SL EoS).^[157] A recent paper also compares the PC-SAFT and SL EoS approaches, and shows that the enhancement of ethylene concentration in the amorphous phase of the polymer due to the presence of n-hexane as an ICA cannot alone explain the increase in the reaction rate observed experimentally during the early stages of a semi-batch reaction.^[158] It appears that the addition of the ICA also impacts the diffusion of ethylene and reduces resistance to mass transfer at the start of the reaction. However a review of the literature reveals that one of the major factors impeding our ability to accurately model these effects (and thus to optimise processes employing ICA) is a lack of data for systems with 2 or more penetrants. Again, it is beyond the scope of the current article to delve into this issue further, but our group hopes to at least partially resolve this problem in the coming years.

4.2 Rate of reaction

A patent application jointly filed by Nova Chemicals and Ineos Europe^[159] is one of the first instances where the inventors explicitly claim to use an ICA to increase the space-time yield of HDPE production. What is important here is that one of the example polymerisations is performed in a semi-batch reactor. This means that the addition of the ICA (in this case hexane, c.f. Figure 18), has a physical effect that causes the observed productivity to go up at constant conditions, and this rate increase is not due to improved heat transfer. Figure 18 shows the impact of adding different amounts of hexane as an ICA to a semi-batch laboratory homopolymerisation of ethylene. The impact of adding hexane is clear: the reaction rate is persistently (and reproducibly) higher over the course of the polymerisation.

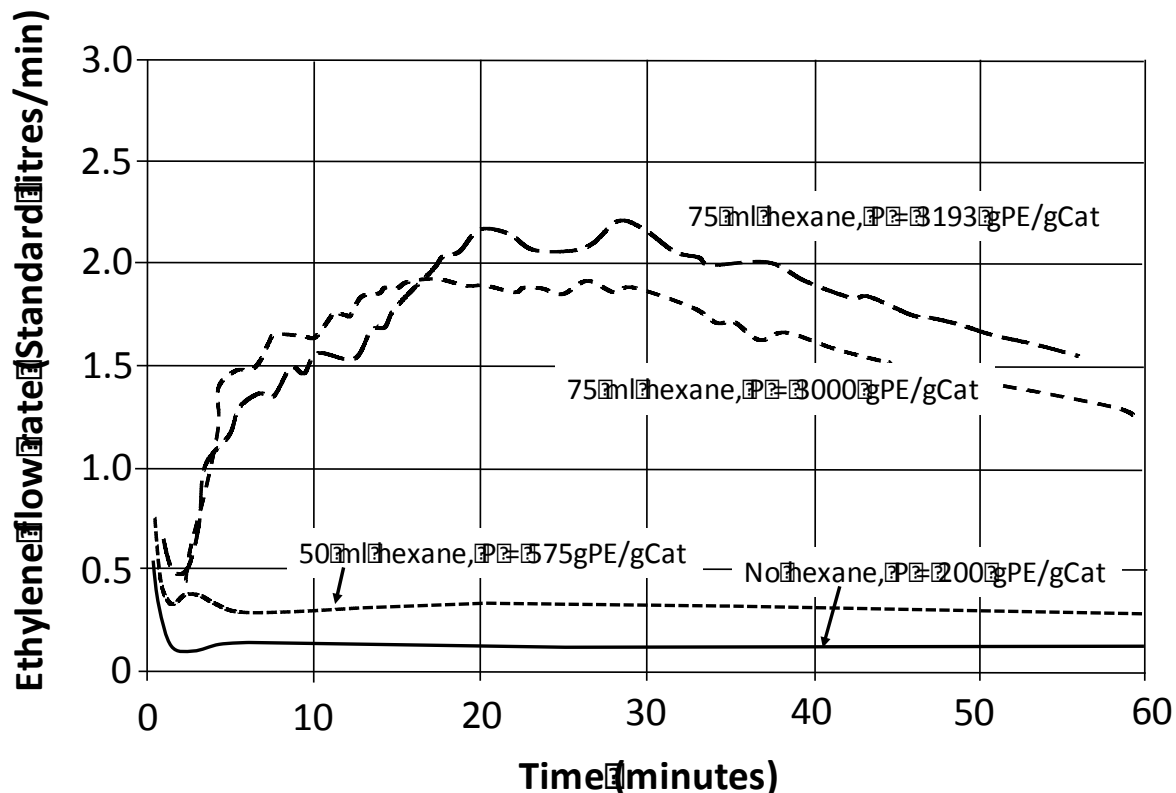


Figure 18. Impact of adding different quantities of hexane to an ethylene homopolymerisation at constant pressure and temperature in a semibatch laboratory reactor. $T = 85^{\circ}\text{C}$, $P = 13.6$ bars ethylene, 3.4 bars H_2 .^[159]

Figure 19 shows the increase in the productivity of a 3-hour polymerisation of ethylene from this patent in a stirred bed reactor having a continuous gas stream. The increase of productivity due to the addition of isopentane is clear, and similar for 2 different catalyst systems. It is explicitly suggested in reference [159] that this increase in the rate of polymerisation (and of the space time yield) is linked to the swelling of the polymer by the vaporised ICA. No further interpretations are proposed in [159], but as we shall see below, this is certainly on the right track. Referring back to Figure 19, it can be seen that the rate of polymerisation increases for both of the catalysts evaluated in Example 2 of the cited patent applications, however the response appears to be stronger for one catalyst than for the other.

This observation is in line with an interesting note that can be found in a patent to Hagerty et al.^[160] While the Hagerty et al. patent focuses on avoiding conditions where stickiness becomes an issue, the authors clearly mention that they observed “that it is possible to reduce operating temperatures and actually increase maximum production rates”.

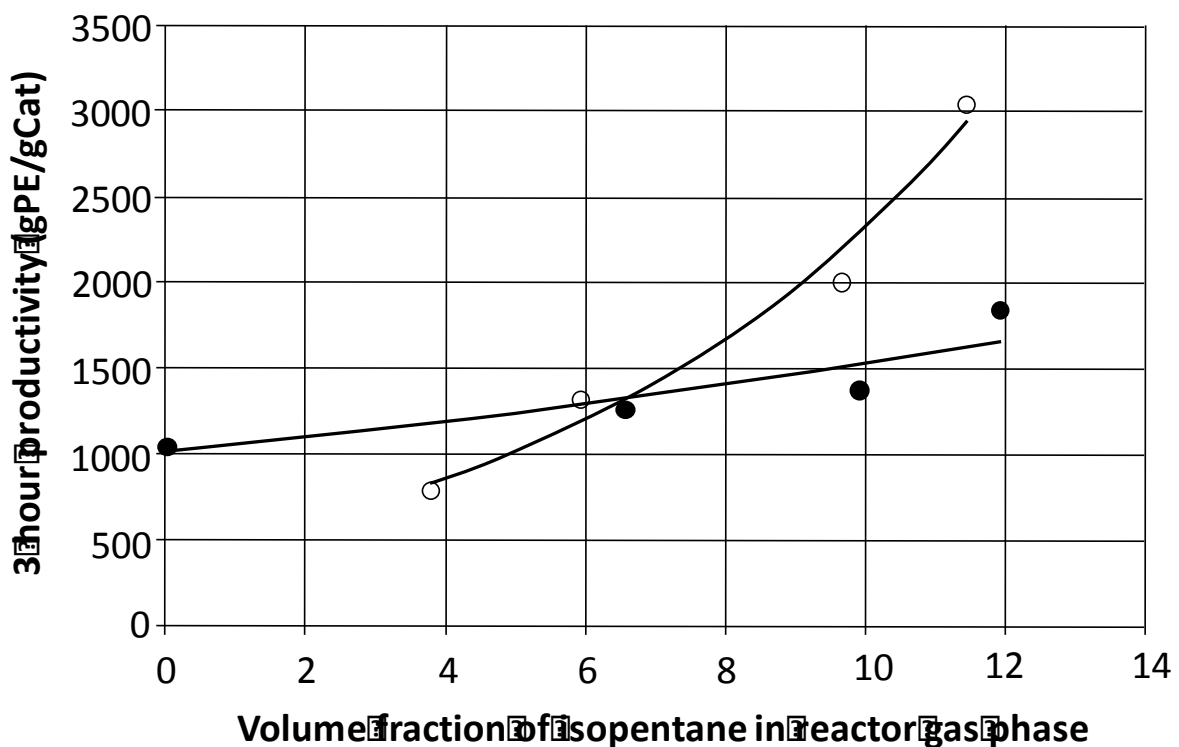


Figure 19. Impact of adding isopentane to 3 hour productivity for 2 different commercial catalysts in a horizontal stirred bed reactor with continuous gas flow. Temperature is 96°C , 14 bars of ethylene, vaporised isopentane.^[159]

While the authors of reference [159] did not specifically mention the cosolubility effect, it is quite likely that this lead to the increase in the polymerisation seen in Figure 18 and Figure 19. Later patents and applications seem to integrate the cosolubility effect

directly into the control of a reactor. For instance, it has been shown that it is important to consider the impact that the alkanes have on the concentration of reactive species in the amorphous fraction of the polymer, and that the ICA themselves can have an impact on the amount of amorphous material present in the reactor under certain conditions.^[161] They propose to use (unspecified) process models to control the levels of reactive species in the amorphous phase of the polymer particles that take into consideration the concentration of monomer, comonomer, hydrogen and ICA on the solubility of the different species. A later patent application also explicitly states that the ICA increases monomer concentration, and this in turn controls the rate as shown above.^[170]

Returning briefly to reference [145], the inventors clearly state that they use ICA (in their patent C4-C7 hydrocarbons) as sorption enhancers, which helps to increase the production rate. Furthermore, they propose a mixture of ICA to improve the gas phase heat capacity, enhance sorption and promote the swelling of the polymer (in the sense of changing the viscoelastic properties). According to their patent, in addition to nitrogen for regulating the pressure, ethane and propane are preferentially used to improve the heat capacity, butane to enhance sorption, and isomers of pentane are used to modify the viscoelastic properties of the polymer. In a similar vein, Namkajorn et al.^[162] showed quite clearly that the heavier the alkane, the more positively it enhances the polymerisation rate (implicitly assuming that the heavier alkanes have a greater impact on the cosolubility effect). Thus, making a distinction between alkanes in terms of specific roles is probably a bit of a stretch, but this patent does show that selecting mixtures of alkanes allows one to fine tune different properties of the feed stream, and to find a balance between increasing rate, increasing heat transfer and influencing the particle morphology.

As mentioned above, heavier alkanes will have a stronger influence on the melting behaviour during the polymerisation (e.g. lower MIT than lighter alkanes), and compounds like pentane will soften PE more than propane.^[64] This implies that the heavier compounds will most likely have a stronger impact on the viscoelastic properties of the polymer in the reactor, and thus on morphology and fines generation (see above). A related patent application showed the trade-offs of the composition of a mixture of ICA between stickiness and production rates.^[163] It can be seen from Figure 20 that 26.4 mol% of n-butane, 6.6 mol% isopentane plus 13.2 mole percent n-butane, and 13.2 mol % of isopentane alone both give the same for estimated sticking temperature (see above for discussion and reference [129] for measurement method) of approximately 75.5 °C, however the different mixtures have different dew point approach temperatures, and will swell the polymer differently, giving different cosolubility effects, and therefore different productivities.

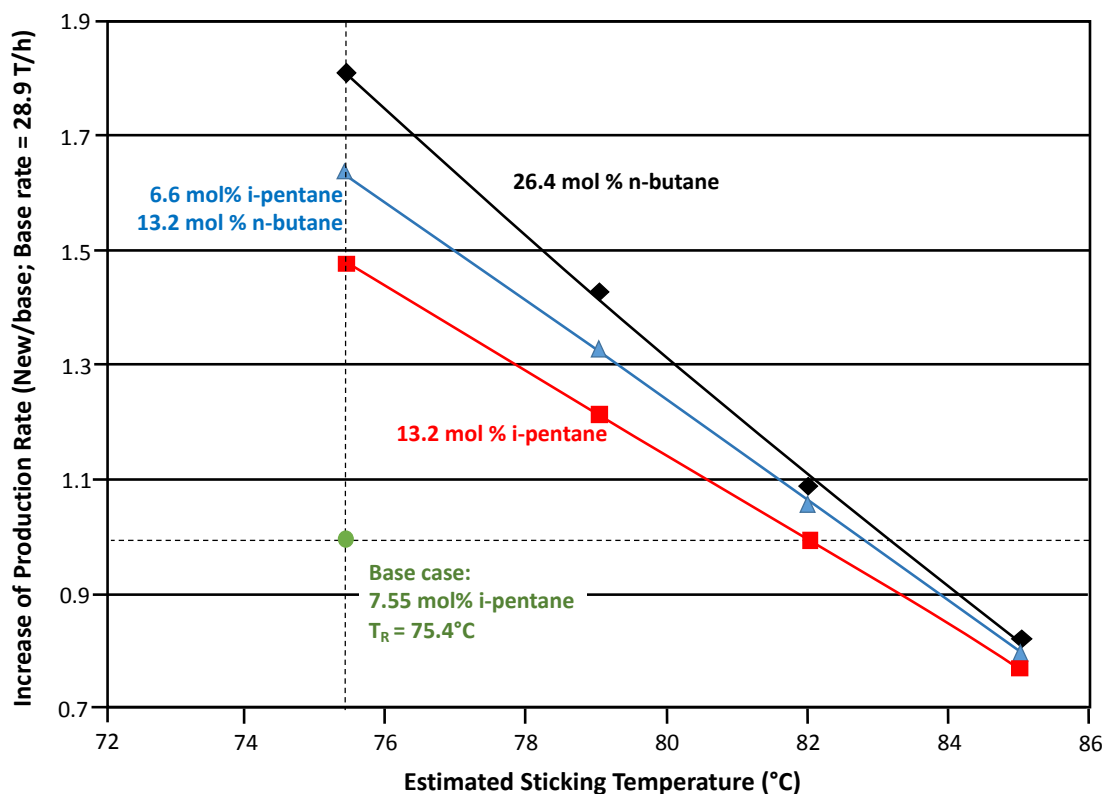


Figure 20. Production rate as a function of sticking temperature^[129] for different mixtures of ICA. Adapted from reference [163].

With this in mind it is tempting to extend this analysis to explain the comonomer effect. This well-known effect refers to the tendency of a copolymerisation of ethylene with a small amount of an α -olefin comonomer to polymerise much faster than the same system with ethylene alone. After all, it has been shown that comonomers swell polyethylene just like alkanes do.^[144] A recent study tried to validate this by comparing ethylene homopolymerisation in DM (i.e. no alkane, no alkene), in SDM (addition of ICA) and the equivalent copolymerisations (addition of α -olefin with same number of carbons.^[164] Figure 21 (red curves) show the impact of adding various amounts of n-pentane to the gas phase of a semi-batch reaction. The relative rate shows the enhancement of adding the ICA (SDM/DM rates). The blue curves show the rate of copolymerisation of ethylene and equivalent quantities of 1-pentene. It can be seen that at 1 bar, the rate of copolymerisation is higher than that of the homopolymerisation in the presence of the equivalent amount of n-pentane. As the concentration of n-pentane increases, the rate of homopolymerisation increases as one expects from the explanations offered for the cosolubility effect. However as the 1-pentene levels increase, the opposite effect is observed; the relative rate, while always higher than the DM polymerisation (the relative rate is always greater than 1), decreases. If one assumes that the cosolubility effect of 1-pentene will be similar to that of n-pentane this implies that low levels of 1-pentene can give a “boost” greater (or at least similar) to that expected from the cosolubility effect, but that as the comonomer concentration increases, the more slowly polymerising comonomer actually slows down the polymerisation rate in a manner that counteracts the cosolubility effect. In other words, a significant amount of work still remains to be done to understand the comonomer effect in ethylene polymerisation, and that the cosolubility effect alone cannot explain it.

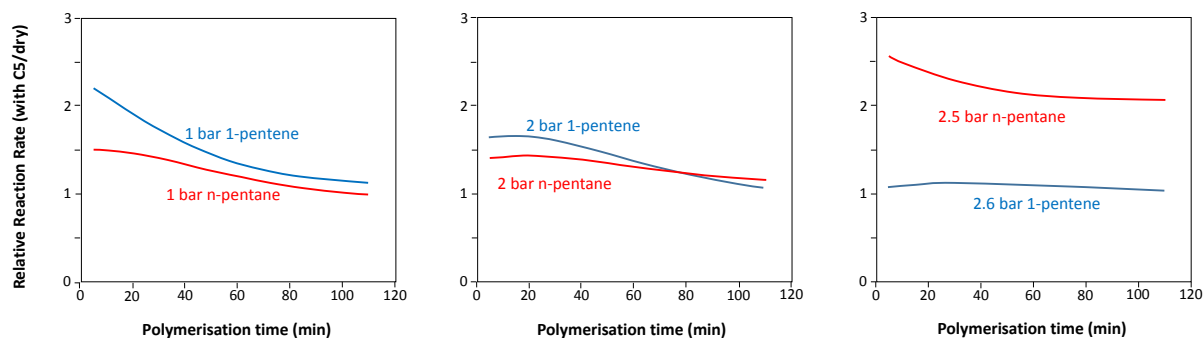


Figure 21. Relative polymerisation rates. The relative rate is that of ethylene polymerisation in the presence of equivalent amounts of 1-pentene or of n-pentane divided by the rate of homopolymerisation in dry mode. Polymerisation at 7 bars ethylene, no hydrogen, 80°C. Adapted from reference [164].

Finally, it has also been shown recently that changing the temperature of the polymerisation when using super dry mode can impact the observed polymerisation rates differently than in dry mode.^[165] As expected, Figure 22(a) shows that when homopolymerising ethylene in DM, increasing the temperature from 70°C to 90°C leads to higher observed rates of polymerisation. However, in SDM with n-pentane as the ICA, the effect is exactly the opposite. Adding 2.5 bars of n-pentane at 70°C leads to an increase of approximately 3 times (c.f. Figure 21). As the increases from 70°C to 90°C, the observed rate of polymerisation actually decreases. This counter-intuitive result was shown to be due to the fact that as the temperature increases, the concentration of ICA in the amorphous polymer decreases, leading to a much less significant enhancement due to the cosolubility effect.

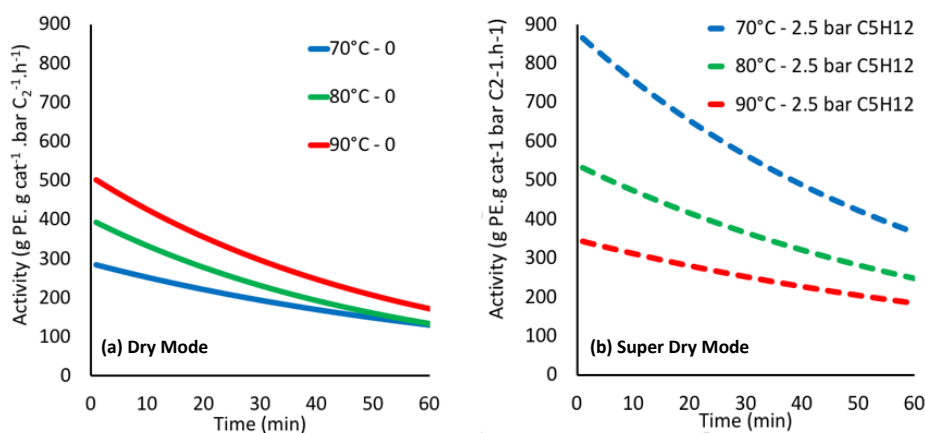


Figure 22. The impact of changing polymerisation temperature on the rate of homopolymerisation in (a) dry mode, and (b) super dry mode. Pressure 7 bar ethylene, no hydrogen, commercial Ziegler-Natta catalyst.

4.3 Molecular weight and other properties

A relatively small number of patents discuss directly the fact that the addition of a chemically inert alkane can in fact have significant consequences on the inherent rate of polymerization, all other things remaining equal. One of the first patents to clearly

mention the impact of alkanes on the aspects other than heat removal and stability what that of Goode et al.^[62], who noted, almost in passing, that in order to maintain constant melt index when increasing the amount of ICA present in the reactor, it was necessary to adjust the hydrogen concentration upward; i.e. more alkanes = higher molecular weight.

In a patent published in 2002, Maddox and Williams ^[166] claimed that the injection of an inert alkane (preferably pentane in their examples) in a gas phase polymerisation catalysed by an activated metallocene improved the observed catalytic activity (Ziegler Natta catalysts were mentioned nowhere in the document). The authors cite a series of patents for both dry and condensed mode cooling, and indicate that the “activator” in their patent is injected in the same way and in the same quantities as an ICA in condensed mode cooling – leading one to suspect that the authors saw that, contrary to what one might expect, the catalytic activity was higher in the presence of the ICA. A very short time later, a patent from Mitsui Chemicals explicitly claimed to use ICA levels in the reactors of a bimodal 2 (or 3) reactor cascade as a means of controlling the physical properties of an LLPDE (ethylene/1-hexene).^[167] The levels of 1-hexene and hydrogen in the different reactors are not specified, but the authors claim that increasing the isopentane concentration in the second reactor allows one to obtain narrower MWD than in cases where no isopentane is used.

In a similar vein, a patent to Univation Technologies also claims the use of different levels of condensable fluids in the reactor to control the width of the chemical composition distribution.^[168] Here specific values of composition are noted for the different examples. Interestingly enough, running an experiment with condensed isopentane does indeed give a narrower composition distribution than without. *However*, it should also be noted that the inventors changed more than just the isopentane levels – the 2 examples are summarised in Table 4. In this table, the term $T_c < 30^\circ\text{C}$ is a measure of the width of the copolymer composition distribution, indicating the percentage of polymer that has crystallized out of solution in CRYSTAF analyses. The lower this value, the less polymer has crystallised out at 30°C , and the narrower the distribution is said to be; meaning that the composition distribution is narrower in the presence of pentane for similar hexene levels. The similarity in densities in the 2 examples presented in Table 4 (and in the other examples in the patent) do not allow us to conclude that the presence of isopentane significantly changes the hexene uptake. It is also very interesting to notice that in Example 2 of this patent, despite having higher levels of hydrogen in the gas phase, the molecular weight is higher (lower melt flow index – MFI) than in example 3. This was noted by the inventors who suggested that ICA could also be used to control the molecular weight distribution. It should not be forgotten here that adding isopentane will increase the rate of polymerisation through the comonomer effect, which will decrease the average residence time of the reactor.^[90] That means that the polymerizing particles will spend different amounts of time in the reactor in Examples 2 and 3, and thus probably have a very different hexene uptake, which could also explain the differences noted. In fact, this patent example serves to illustrate the complexity of potential changes in reactor behaviour when running in condensed mode with respect to running in dry mode (and also illustrates that a significant amount of fundamental science and engineering remains to be done in order to allow us to better understand what is happening in commercial reactors).

Table 4. Impact of isopentane on polymer properties.^[168]

	Example 2	Example 3
Bed Temperature (°C)	77	77
Partial Pressure Ethylene (psia)	220	220
Hexene/ethylene ratio (C6/C2)	0.0138	0.0148
H ₂ concentration (ppm)	288	235
Isopentane (mol %)	6	0
Density (g/cm ³)	0.916	0.917
MFI (I ₂ , g/10 min.)	0.9	1.4
T _c < 30°C	4.8	10.8

Other groups have used different levels of ICA to control the relative amounts of high molecular weight (HMW) polymer in a bimodal PE (single reactor).^[169] The supported catalyst in the example of reference [169] carries 2 types of active sites, one metallocene for the low molecular weight fraction (LMW) and a non-metallocene Group 4 metal catalyst for the high molecular weight fraction (HMW). It is demonstrated that changing the isopentane concentration changes the productivity of the HMW producing catalytic sites, but not the LMW sites. The reason for this is not stated, but it is highly possible that the HMW sites (non-metallocene) are sensitive to changes in the concentration of ethylene, and that the LMW sites are not (this is not uncommon for metallocenes that have high rates of transfer to ethylene, so one suspects that this is the case here). As we will discuss below, the so-called cosolubility effect where an inert alkane heavier than ethane can enhance the solubility of ethylene is the most likely explanation for this type of observation. Furthermore, dropping from 10.5 wt % isopentane in the reactor feed to 5.6 wt%, causes the productivity to drop from 6000 kg PE/kg catalyst to just over 5000 kg PE/kg cat (and a gain in activity noted if the change of isopentane level is in the other direction). An important point to make is that in the example they present it does not matter whether or not the pentane is in a condensed state or a vapour state for this component to influence the MWD.

Recent patent applications focused on the impact of the ICA on the molecular weight distribution (or melt index, MI) ^[170,171,172]. In reference [170], it is suggested that the increase in ethylene concentration at the active sites due to the presence of the ICA is responsible for the increase in the molecular, and that if this can be quantified, it should be possible to counter any increase in the molecular weight due to the cosolubility effect by changing monomer pressure in the reactor (eventually in combination with changes in the residence time and/or temperature). Namkajorn et al.^[173] also observed significant increases in the molecular weight and molecular weight distribution when small quantities of isopentane or n-hexane were added. However, they observed (in the absence of hydrogen) that the increases in the weight average molecular weights were greater than one might expect based on the cosolubility effect.

Interestingly enough, it has also been observed that the evolution of the MI provoked by the addition of an ICA is not necessarily instantaneous, but rather observed to take place over a period of several tens of minutes to hours in a commercial process.^[172] This in itself is not necessarily surprising as the residence time distribution of the powder in the reactor is akin to that of an ideal CSTR, so it could take several residence time

distributions for such a change to reach a new steady state in terms of product properties.

5 Modelling of reactors and single particles in condensed mode operation

The number of studies dedicated to modelling condensed mode operation is surprisingly limited given the commercial importance of the processes employing this technology, and given the numerous (far too numerous to cite) papers on modelling fluidised bed reactors in general.

A series of three papers from 1997 presented an analysis of cooling in condensed-mode processes, but essentially focused on the multicomponent condensation in an external heat exchanger.^[174,175,176] None of them actually included a model for the reactor, or looked at the impact of compositional changes on the polymerisation rate or properties. Around the same time, a group from Aspen Technology presented a rapid analysis of the impact of going from dry to condensed mode in the same plant (the authors used the term supercondensed mode, but only considered feed flows containing around 10 wt% liquid, which is standard condensed mode according to our definition).^[177] They approximated the FBR by an ideal continuous stirred tank reactor (CSTR; a reasonable first approximation), and used a binary version of the SL EoS to calculate the individual component solubility in PE. The simulations showed that increasing the heat removal rate obviously allows one to increase the productivity. In addition, and perhaps more interestingly, they also demonstrated that because of the reduced residence time of the reactor (from 5 hours down to under 2 due to the higher rate), slowly deactivating catalysts showed an increase in ash content.

Other authors ^[178,179] used more sophisticated FBR and kinetic models, but not a thermodynamic model that accounts for the cosolubility effect, to arrive a similar conclusions; increasing the liquid in the feed stream (assuming complete and instantaneous evaporation) allows one to remove more heat and to increase the safe operating window of the reactor. It was also shown that decreasing the reactor inlet temperature also increases heat removal and further adds to the potential for increased production rates.^[179] Zhou et al. relaxed the assumption of instantaneous evaporation of the liquid to extend the analysis of CM in an FBR to look at temperature profiles in the reactor.^[72] They showed that increasing the liquid levels of the feed and/or decreasing feed temperature could lead to a more extended cold temperature zone in the reactor (c.f. Figure 10a), and this could impact properties such as the MWD (c.f. Figure 10b).

Pan et al. used an even more complex model incorporating population balances for particle size, droplet evaporation as a function of droplet size (with a droplet size distribution), and a computational fluid dynamics model to understand how evaporation impacts bed expansion.^[180,181] Their analyses are in agreement with those of Zhou et al.^[72] in terms of the evolution of temperature profiles in the reactor.^[180] In addition, the addition of i-pentane to the fluidizing gas also has a significant impact on bed hydrodynamics and on the solids content; the solids content increasing as the pentane levels increase (see discussion on FBD/SBD in section 3).

The models all seemed to qualitatively capture the different trends that were discussed in previous sections. None of them are proposed as comprehensive models, and given the computing power that would be required to look at hydrodynamics, the PSD, the MWD, bed profiles etc., this is not unreasonable. The main shortcomings of the reactor models is the fact that they do not use thermodynamic data that allow one to include the impact of the cosolubility effect. To the best of our knowledge, the only work that does so is a recent paper from our group.^[90] Alves et al. used a modified SL EoS to look at the effect of adding propane or butane as an ICA during the homopolymerisation of ethylene in SDM, and to account for the cosolubility effect. They used patent data to fit a simplified kinetic model to describe the rate of polymerisation in DM, fitted the SL EoS model parameters using literature data, and treated the FBR as an ideal CSTR. The simulations agreed well with patent data^[182]. The significance of including the cosolubility effect on predictions of polymerisation rates and reactor residence times was clear, and the authors also demonstrated that even if one accounts for the presence of an ICA in terms of an increased heat capacity, using binary SL EoS to calculate ethylene solubility will lead to a significant error in terms of over predicting residence times, and poorly predicting the PSD. On the other hand the authors did not attempt to look at the impact of ICA on polymer properties, nor did they include a single particle model in their solution.

In terms of single particle modelling, very few papers have explicitly attempted to examine the impact of the presence of an ICA on particle behaviour. One of the first to do so (not surprisingly) were Hutchinson and Ray.^[183] They proposed to look at particle overheating using a simplified particle model that neglected internal material and energy gradients, and did not account for sorption effects. It was assumed that the growing polymer particles are coated by a thin layer of liquid that evaporates as the particles polymerise and heat up. They showed that if this representation were correct, only a very small fraction of the heat generated by the particle is actually removed by evaporation of said liquid film for small, hot particles. Another study used a similar approach several years later, including internal gradients via a polymer flow model (PFM).^[81] These authors reached a similar conclusion to that of Hutchinson and Ray; i.e. negligible cooling of particles due to the evaporation of a thin film, and most of the heat of polymerisation is evacuated via convective heat transfer. It is not clear how realistic the notion of a thin film of liquid on the surface of particles is. One expects that, contrary to processes such as fluid catalytic cracking where the aim is to wet the particles, the idea in a polyethylene process is to not wet them so as to avoid the formation of liquid bridges^[184] that could lead to agglomeration. Regardless, it appears that this type of evaporation would be negligible were it to occur.

In a different vein, Alizadeh and McKenna^[185] implemented a simplified single particle model using the SL EoS to investigate the order of magnitude of the impact that sorption and evaporation of hexane as an ICA would have on particle temperatures. They neglected heat and mass transfer, and assumed that the concentrations of reactive species in growing particles were in equilibrium with those in the bulk phase. It was shown that evaporation of sorbed hexane had a negligible impact on particle temperature under normal conditions of fluidisation. However, in cases where local gas-particle velocities were reduced, the particles could be as much as 5-12°C cooler if hexane were present in the reactor. The amplitude of the temperature decrease

depended on reaction rate and particle size, with the effect being more pronounced for smaller, hotter particles.

6 Conclusions

This review has shown that a conceptually simple change in reactor operation – the addition of ICA (condensed or not) – can have a profound impact on the heat removal capacity of an FBR used to produce PE as intended. It can also change other things very important things in the reactor as well:

Bed stability and particle agglomeration can be negatively impacted by the increased stickiness of (hot) plasticised powders. Significant industrial effort has clearly gone into detecting and resolving said problems. In the current article we have expressly avoided talking about the control schemes that can be found in the literature to avoid bed stability and ensure smooth grade changes, but there are at least as many as we have discussed in terms of detecting and avoiding stickiness-related problems.

The thermodynamic impact of ICA (and comonomers) on the solubility of different species is also very important, but very poorly understood. Even in very simple systems such as PE-ethylene-ICA, if one does not account for the cosolubility effect of the ICA on ethylene, then one runs the risk of being unable to predict its impact on reactor residence time and heat production rates. In addition, if one uses incorrect values for monomer concentrations in the polymer phase during polymerisation, it is possible that estimates of rate constants, reactivity ratios etc. will be erroneous. We might think for instance that adding butane to a reactor somehow changes the propagation rate coefficient if we do not include the cosolubility effect in the estimate of the propagation rate constant for ethylene.

Adding ICA also appears to influence (positively) fines generation, and, according to most of the patents discussed above, the bulk density of PE reactor powder. Presumably this is due to the plasticisation of the polymerising particles, rendering them more deformable.

Product properties such as the molecular weight distribution seem to be influenced by the addition of ICA, both through the change in the material properties of the polymer (solubilities, deformability, etc.) at a given temperature, but also through the impact that condensed ICA can have on the temperature profile in the reactor.

In addition to all that, each different ICA will have different impacts on the process, making it very difficult to identify an “optimal ICA composition”.

Finally, our understanding of how to model concentration and diffusion in the amorphous phase of PE is very limited. A review of the academic literature (and private discussions with many people at production sites) lead to the conclusion that we are severely lacking data that can be used to strengthen or improve existing models. Without such thermodynamic models, it will be very difficult to build more refined process models that help us to better predict and control polymer properties at the level of the reactor. Much remains to be done!

7 Acknowledgements

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