

IMPROVED UNDERSTANDING OF THE IMPACT OF ALKANES WHEN USING CONDENSED MODE COOLING FOR PE PRODUCTION

Timothy F.L. McKenna, Arash Alizadeh, Rita Alves, Fabiana N. Andrade, C2P2 – LCPP Group, UMR5265 CNRS, ESCPE Lyon, Université de Lyon, Villeurbanne, France

Abstract

Condensed mode cooling, the technology of using induced condensing agents (ICA) to cool fluidised bed reactors during the polymerisation of ethylene in the gas phase is a widely used technology. ICA are usually low molecular weight alkanes, and thus chemically inert. However, in addition to influencing the heat removal capacity, they can also have a significant impact on reaction rate, powder morphology, molecular weight, and other quality related parameters in unexpected ways.

Introduction

It is probable that at least 30 million tonnes of polyethylene (PE) will be produced in 2019 in gas phase fluidised bed reactors (FBR). With the exception of the new Hyperzone technology, FBRs are the only gas phase reactors that allow us to remove the heat generated by this highly exothermic polymerisation. In fact, due to an ever-increasing demand for PE, if one wishes to optimise the productivity of a given production line, it is becoming more and more important to be able to remove the reaction heat, on the order of 10 to 90 megawatts (MW) [1]. A recent review has discussed the problems associated with heat removal in gas phase reactors and underlines the point that many modern processes used either condensed mode cooling, or what can be termed “super dry (SD) mode” [2]. In a process run in either of these two modes, the feed to the reactor contains not only nitrogen, hydrogen, ethylene and comonomer(s), but also compounds referred to as induced condensing agents (ICAs), typically C3-C6 alkanes. In the case of condensed mode operation, the feed stream is cooled to below its dew point; in SD mode, the feed stream can contain similar compounds, but at a temperature above the dew point. In condensed mode, the feed stream injected into the reactor contains small droplets that evaporate rapidly to help remove a good portion of the heat generated in the reactor. After vaporisation, or directly in SD mode, the presence of ICA in the vapour phase of the reactor increases the heat capacity of the gas flowing through the reactor; this too leads to a considerable increase in the amount of heat removed from the reactor with respect to dry mode (i.e. operation of the FBR without ICA).

ICAs are chemically inert in the sense that they do not have any influence on the behavior of the active sites. However, it also turns out that while chemically inert, adding ICA can change the free volume of the polymer

phase [3]. The end result of this is that an ICA absorbed in the amorphous phase can enhance the concentration of monomers lighter than itself (and decrease that of species heavier than itself) [4]. In other words, a physical effect can manifest itself in ways that could be interpreted as chemical effects. Different ICA act differently on the polymer [5] and can have a significant impact on the particle morphology and molecular weight [6].

Discussion

As an example of some of the interesting, somewhat unexpected behaviour, let us consider Figure 1 (adapted from Andrade et al. [7]). In Figure 1 (a) it can be seen that, as expected, the rate of polymerization of ethylene alone increases as the temperature of the reaction increases. However, when exactly the same polymerisation is performed in the presence of n-pentane, the situation is quite different. Here the observed reaction rate appears to decrease as the temperature of the reaction increases. This behaviour is quite reproducible and also observed when hexane is used as the ICA [7].

Clearly, this highly non-ideal thermodynamic behaviour requires sophisticated thermodynamic models in order to capture and predict phenomena such as the “cosolubility effect” (the tendency for heavier components to enhance the sorption of lighter ones, and that of lighter ones to be antisolvents for heavier ones) [8]. Several models have been proposed for this purpose [9], but it appears that equations of state using either a lattice-based or perturbation approaches are the most suitable for a number of reasons discussed in reference [9]. The Sanchez-Lacombe Equation of State (SL-EoS) [10] is a popular lattice model, and the Perturbed Chain – Statistically Associating Fluid Theory (PC-SAFT) [11] is perhaps the most widely used equation of state employing perturbation theory. Both have strengths and weaknesses, but can, with some good data (which unfortunately is quasi inexistent for realistic mixtures of vapours in PE or PP under standard reaction conditions), use adjustable parameters in these models to at least capture the important trends in the cosolubility effect [12].

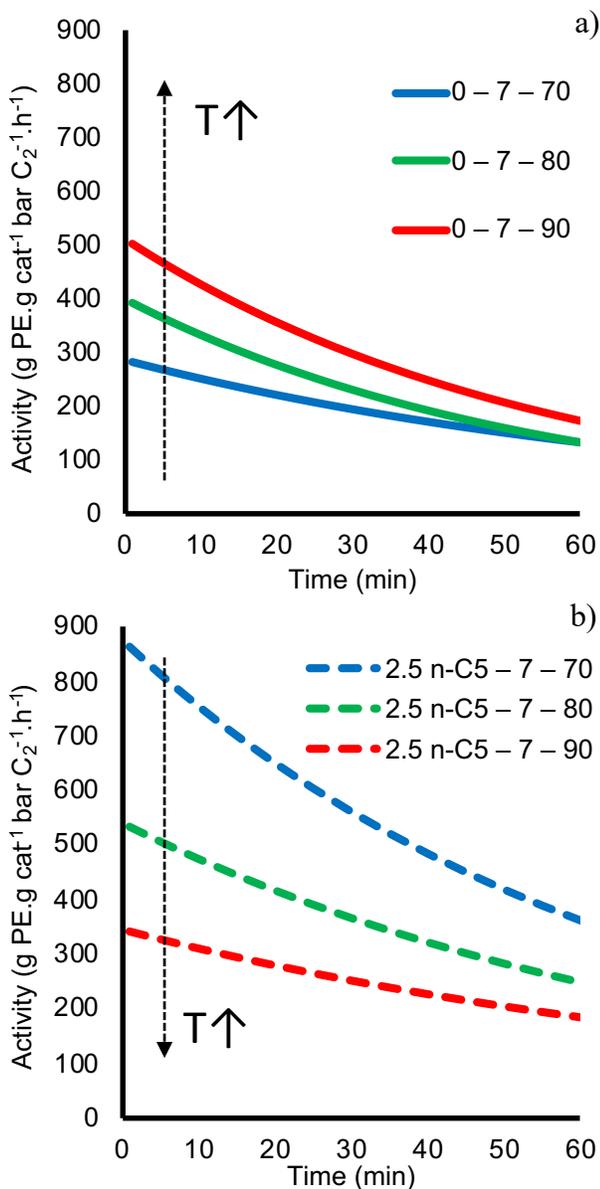


Figure 1. (a) Rate of polymerisation of 7 bars of ethylene in alone as a function of temperature on a commercial Ziegler-Natta catalyst. (b) The same, but in the presence of 2.5 bars of n-pentane. See reference [11] for information concerning experimental set-up and protocols.

Returning to the discussion of Figure 1, we used the SL-EoS to model the solubility of ethylene in binary (ethylene + PE) and ternary (ethylene + n-pentane + PE) systems as a function of temperature and ICA concentration for a fixed pentane pressure of 2.5 bars. The results are shown in Figure 2, where it can be seen that the ethylene solubility in the binary system is a weak function of the temperature (Figure 2a), decreasing, but only a little as the temperature increases. On the other hand, the solubility of ethylene in the ternary system is

a stronger function of the temperature. At a 70°C, the ethylene solubility in the ternary system is about 20% higher than in the binary system for a given ethylene pressure. So (as we can see in Figure 1) this causes the reaction rate to go up significantly in the ternary system. This is the cosolubility effect. However, as the temperature rises, the pentane solubility decreases, so the magnitude of the cosolubility effect decreases and the reaction rate (in this case, with this catalyst and this pentane concentration) actually drops in a way one would not necessarily expect. Note that this does not mean that adding any ICA at any concentration will lead to a rate decrease as the temperature increases (that would be nice in terms of preventing runaways!). More data on cosolubility and experimentation is required to be able to draw more general conclusions.

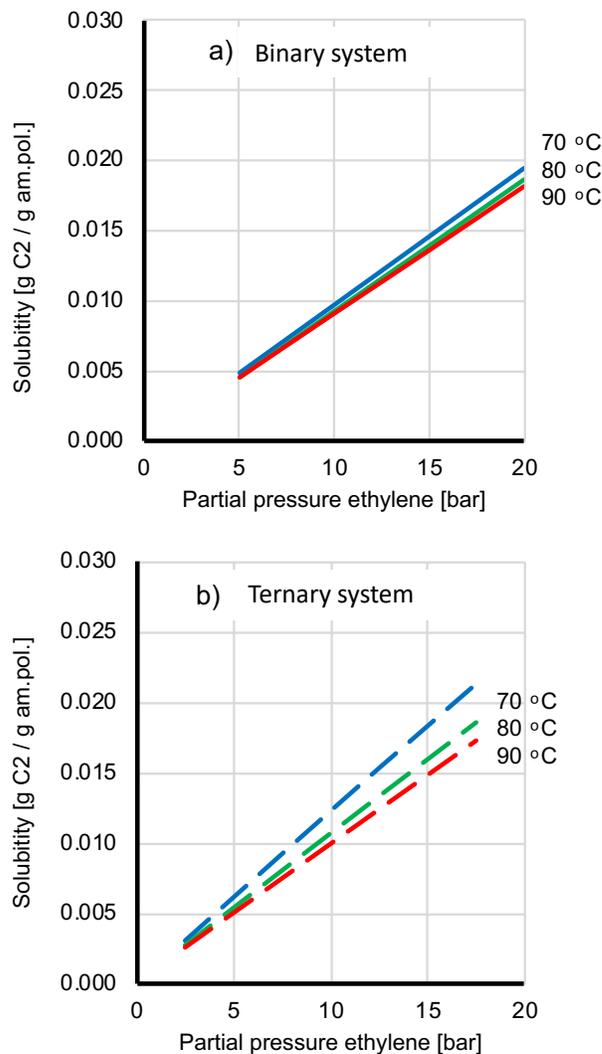


Figure 2. The solubility of ethylene in amorphous PE as a function of temperature and ethylene pressure. Top is the binary ethylene-PE system, bottom is the ternary ethylene-pentane-PE system at 2.5 bars of n-pentane. [7]

The significance of using the correct thermodynamic model can also be seen in Figure 3. This figure represents the output of a relatively simple model of an FBR operating in dry mode (no ICA) and in SD mode [13]. The reactor is modelled as a CSTR at steady state, the polymer is assumed to be at equilibrium with the vapour phase, no mass transfer resistance is considered at the level of the polymer particle, polymerisation rate is independent of the particle size, entrainment and agglomeration are neglected, ternary VLE (ethylene-isobutane-PE) was modelled using the SL-EoS and the temperature of the reactor is uniform and constant. While these might seem to be somewhat restrictive, the model was validated against some operational data from an industrial plant [14] and showed less than 3% error in predicting productivity and less than 15% error in predicting the average residence time of the patent data.

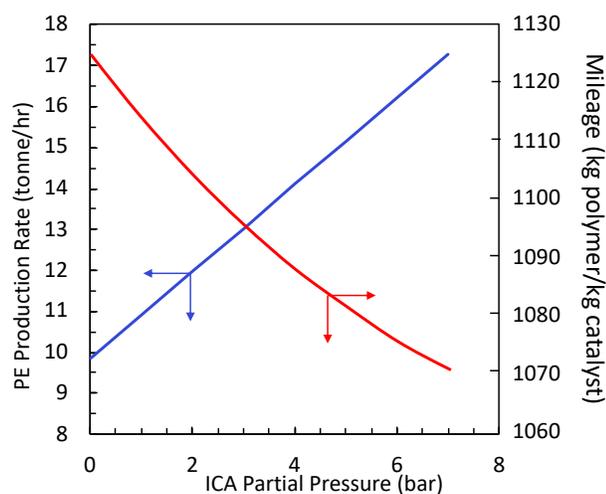


Figure 3. Simulation of the productivity (blue, increasing) and catalyst mileage (red, decreasing) of an industrial scale plant as a function of the partial pressure of iso-butane. Simulation at 7 bars ethylene, 70°C. Other details available in [13].

The results of these simulations show several interesting trends. First of all, if one does not account for cosolubility effects, the production rate of 10 tonnes/h would remain constant, regardless of the amount of iso-butane in the reactor – in other words a sophisticated multicomponent thermodynamic model is definitely needed. Secondly, it can be seen that even though productivity goes up as a function of the iso-butane content, the catalyst mileage goes down. In other words, we are producing less polymer per kilo of catalyst. This is because the cosolubility effect leads to an increase in the observed rate of reaction, but in order to keep the bed volume constant we are obliged to remove the polymer from the reactor at a faster rate. Obviously, economics favours using some form of condensed mode cooling, but this is a trade-

off that needs to be considered. Furthermore it is important to pay attention to the impact of this type of behaviour on the ash content of the final product.

In addition to influencing reaction rates and reactor performance, the presence of different amounts and types of ICA can have an impact on the physical properties of the final polymer. It has been shown in [6] that different levels of ICA can have a significant impact on particle morphology, and on the molecular weight distribution. For instance, Figure 4 shows the dependence of the weight average molecular weight (M_w) of different HDPE produced on the same commercial catalyst at different temperatures, and with different ICA close to the dew point of the ethylene-ICA mixtures. It can be seen here that M_w decreases with temperature (as expected), but significantly increases in the presence of ICA, with different ICA having different impacts.

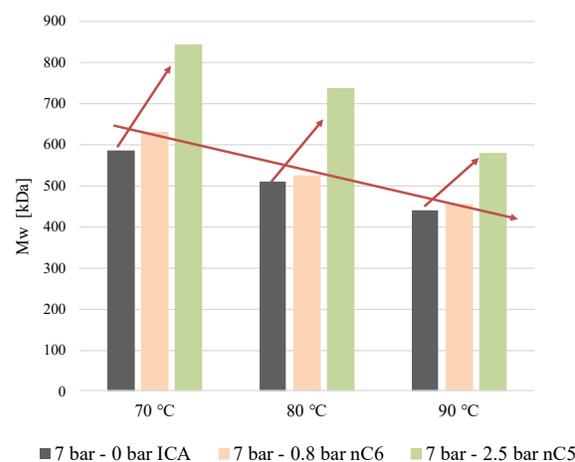


Figure 4. The evolution of the weight average molecular weight of HDPE produced at a total pressure of 7 bar, with variable amounts of different ICA and no hydrogen. [7]

And in a final remark, as yet unpublished data from our group suggests that the complex thermodynamic interactions at play can also influence the copolymer composition in the case of LLDPE production.

Conclusions

In conclusion, it should be clear that a far deeper understanding of the impact of alkanes on the polymerisation of ethylene in the gas phase is really needed if we are to avoid simply modifying things by trial and error.

It is easy to imagine that if a given ICA influences the solubility of ethylene and of butene differently, then if we do not have good solubility data, estimation of kinetic constants such as the reactivity ratios needed to predict copolymer composition will be simply wrong – we can

clearly not use a binary model to calculate the concentration of these two species independently!

A number of the phenomena reported here can be modelled (at least semi-mechanistically) by adapted free-volume based models. However, much like the SL-EoS and the PC-SAFT EoS, these models do not explicitly account for variations in the composition of semi-crystalline material, so extensive data is required so that we can fit certain model parameters. And to be very clear, this data is extremely scarce in the literature. One can find a great deal of data for binary systems, a very limited amount for ternary systems, and zero (in so far as we can tell) for higher order systems that are representative of real reactor compositions.

Finally, up to this point we have only discussed gas phase polymerisations, but it seems evident from the examples shown here, that similar information is required for slurry systems!

References

1. J. Soares, T.F.L. McKenna, "Polyolefin Reaction Engineering," Wiley-VCH, Mannheim, Germany, (2012)
2. T.F.L. McKenna, *Macromol. React. Engng*, doi: 10.1002/mren.201800026 (2018)
3. M.A. Bashir, V. Monteil, M. Al-Haj Ali, V. Kannelopoulos, T.F.L. McKenna, *Macromol. Chem. Phys.*, **216**, 2129 (2015)
4. A. Alizadeh, M. Namkajorn, E. Somsook, T.F.L. McKenna, *Macromol. Chem. Phys.*, **216**, 903 (2015)
5. A. Alizadeh, M. Namkajorn, E. Somsook, T.F.L. McKenna, *Macromol. Chem. Phys.*, **216**, 985 (2015)
6. M. Namkajorn, A. Alizadeh, D. Romano, S. Rastogi, T.F.L. McKenna, *Macromol Chem. Phys.*, **217**, 1521 (2016)
7. F.N. Andrade, T.F.L. McKenna, *Macromol Chem Phys.*, **218**, 1700248 (2017)
8. B.J. Banaszak, D. Lo, T. Widya, W.H. Ray, J.J. de Pablo, A. Novak, and J. Kosek, *Macromolecules*, **37**, 9139 (2004)
9. Y. Guerrieri, K. Valverde Pontes, G. Meyberg, N. Costa, and M. Embiruçu, "A Survey of Equations of State for Polymers," 357–402 in *Polymerization*, A. De Souza Gomes (ed), IntechOpen, London, UK, (2012)
10. I. C. Sanchez, R. H. Lacombe, *J. Phys. Chem.*, **80**, 21, (1976)
11. J. Gross, G. Sadowski, *Ind. Eng. Chem. Res.*, **197**, 541, (2002)
12. A. Alizadeh, J. Chmelař, F. Sharif, M. Ebrahimi, J. Kosek, T.F.L. McKenna, *Ind. Eng. Chem. Res.*, **56**, 1168 (2017)
13. R. Alves, M.A. Bashir, T.F.L. McKenna, *Ind. Eng. Chem. Res.*, **56**, 13582 (2017)
14. A. Bragança, A. Morschbacker, E. Rubbo, C. Miro, T. Barlem, A. Mukherjee. US 6864332 B2, 2005